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## Preface

On behalf of the Organizing Committee, I would like to welcome you to MACROMEX 2011 and XXIV Congress of The Mexican Polymer Society (MPS), which is being held at Riviera Maya, in Quintana Roo, México.

In 2008, the Polymer Division of the ACS and the Mexican Polymer Society co-organized the first bi-national US-Mexico Symposium in Polymer Science, MACROMEX 2008, in Los Cabos Baja California. The event was a success due to the high quality of the scientific program and the interactions that emerged from the encounter. To celebrate the International Year of Chemistry, and to continue with fruitful collaborations between the scientific communities of both countries, a second bi-national symposium was planned to take place in beautiful Riviera Maya, in Quintana Roo, facing the Caribbean Sea. Additionally, for this second encounter, a group of renowned invited speakers from Canada will also join us. The goal of the meeting is to exchange ideas, promote collaboration and discuss new trends of polymer science and technology and their impact in the North American region. The Congress has been carefully organized to present the latest developments in North America (United States of America, México and Canada) in the growing field of polymer science and technology.

In the book of abstracts you will find the text of the papers being presented, as well as symposia program and schedule. Electronic abstracts and proceedings can be found at our web site http://www.sociedadpolimerica.mx/. Meeting proceedings are contained in extended abstracts CD.

The book of abstracts and extended abstracts CD are the product of many people's efforts, and I would like to thank all of them on behalf of the MPS. The program would not be possible without the participation of the symposium organizers and the invited and oral speakers. In particular, special acknowledgement is given to the symposium organizers Krzysztof Matyjaszewski, Ken Wynne, Gobet Advincula, César García-Franco, Carmen Scholz, Michael Jaffe, Don Paul, Ángel Licea-Claveríe, Enrique Saldívar, Gabriel Luna, Manuel Aguilar-Vega, Francisco Medellín, Eduardo Mendizabal, Beatríz García-Gaytán, Robin Hutchinson and Michael Cunningham. We have scheduled symposia on Precision Polymer Synthesis; Biomaterials; Self assembly, Nanomaterials and Blends; Advanced Polymer Materials: Optoelectronics and Membranes; and General Topics on Polymer Science.

Grateful thanks are extended to Lesia Linkous for her help during the organization of this Congress. In addition, special thanks are due to Dr. Arturo Zizumbo-López (Instituto Tecnológico de Tijuana), who was responsible for the administration of the official Macromex web page, arranging the book of abstracts and extended abstracts CD and overseeing them along the path to publication, and to Karla A. Barrera-Rivera (Universidad de Guanajuato), who has provided a special and invaluable administrative support.

I believe you will enjoy MACROMEX 2011 and XXIV Congress of the Mexican Polymer Society. This event is part of the International Year of Chemistry. Please join us in the celebration!

Antonio Martínez-Richa President – Mexican Polymer Society 2009-2011

POLYOLEFINS

## DEVELOPMENT OF FLOW INSTABILITIES DURING EXTRUSION OF POLYOLEFINS AND FILLED POLYOLEFINS AS AFFECTED BY PRESSURE-DEPENDENT SLIP AT THE WALL

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#### Abstract

For polyolefins and filled polyolefins the pressure dependence of wall slip velocity can be significant, with slip velocity decreasing with increasing pressure. Since the flow curves characterized during rheometry are subject to wall slip, and since such slip is a function of wall shear stress and pressure, new methodologies are necessary for the characterization of the parameters of pressure-dependent wall slip and shear viscosity. Here an overview of pressure dependence of wall slip in the development of flow instabilities will be made together with comparisons of experimental and numerical analysis results for rectangular slit and tubular dies.

#### **Development of flow instabilities**

The generation of various flow instabilities that affect the quality of the surface and bulk shape of the extrudates emerging out of extrusion dies is a serious bottleneck to the production of extruded articles. Thus, it is very important to understand the causes of such flow instabilities so that they can be minimized or eliminated so that gains in production rates can be made. One of the major parameters to consider is the occurrence of wall slip of complex fluids at the channel walls. It was hypothesized that wall slip of polymers occurs as a function of normal stress/pressure at the wall with wall slip velocities decreasing with increasing normal stress/pressure [1-4]. We have shown earlier that the changes in the wall slip condition along the length of an extrusion die can have significant effects on the development of flow instabilities [5, 6].

In the first study involving pure polymer melts [5] a mathematical model was developed for the timedependent circular tube flow of compressible polymeric liquids subject to pressure-dependent slip at the wall. The mathematical model was applied to a poly (dimethyl siloxane) (PDMS). The parameters of pressure-dependent wall slip velocity and shear viscosity of the PDMS were determined using combinations of small-amplitude oscillatory shear, steady torsional and squeeze flows and were employed in the prediction of the time-dependent circular tube flow behavior of the PDMS. The numerical solutions suggested that a steady tube flow is generated when the flow boundary condition at the wall is stable, that is, either a contiguous stick (or weak slip) or a contiguous strong slip condition along the entire length of the wall. On the other hand, when the flow boundary condition changes from stick (or weak slip) to strong slip at any location along the length of the wall, undamped periodic oscillations in pressure and mean velocity were observed. The experimentally characterized and simulated tube flow curves of PDMS were determined to be similar and the simulation findings for flow stability were in general consistent with the experimentally observed flow instability behavior of PDMS.



Figure 1: Comparisons of experiment versus theory for a PDMS melt under capillary flow: Wall shear stress versus the apparent shear rate for three sets of capillaries with differing diameters: Diamond-0.83mm, square-1.5mm, triangle-2.5mm, filled symbols–unstable, open symbols– stable, symbols with dot inside -- experiment

In a second study involving polymeric suspensions [6] the mathematical model of the time-dependent circular tube flow of compressible fluids subject to pressure-dependent wall slip [1] was applied to the tube flow of polymeric suspensions with rigid particles. The model relied on the apparent slip mechanism for suspension flow (the apparent slip layer is the zone at the wall which consists solely of the binder phase [7] with the additional caveat that the polymeric binder slips at the wall according to a pressure-dependent wall slip condition. The numerical simulations of the tube flow of concentrated suspensions suggested that steady flow is generated when the flow boundary condition at the wall is a contiguous strong slip condition along the entire length of the tube wall. The findings of the simulations were consistent with the experimental flow curves and flow instability data collected on suspensions of the poly (dimethyl siloxane) (PDMS), which itself exhibits wall slip, compounded with rigid and hollow spherical particles in the 10 to 40% by volume range. Increasing the concentration of rigid particles gave rise to the expansion of the range of flow rates over which the flow remains stable, as consistent with the experimental observations.



Figure 2: Comparisons of the experimental flow curve of PDMS suspension ( $\phi$ =0.1) with the numerical simulations: Diamond-D=0.83 mm, square- D=1.5 mm, triangle-D=2.5 mm, filled symbols–points that are predicted to be unstable, open symbols– points that are predicted to be stable, open symbols with crosses experimental data; dotted lines represent the lower and upper bounds of apparent shear rates over which extrudate distortions are experimentally observed.

Having thus established that the pressure dependence of the wall slip boundary condition is of utmost importance in the development of flow instabilities the gained understanding was further applied to other complex fluids. In the following applications to the determination of the pressure dependent parameters of wall slip condition for a concentrated suspension and a gel are demonstrated. The pressure dependence of the apparent slip layer thickness,  $\delta$ , is the mechanism that is further considered in this study.

### Experimental

Two complex fluids were used. The first was a hydrogel of sodium carboxymethyl cellulose, NaCMC (Aqualon 7H4F, Hercules) (Fluid I). An intensive batch mixer (Haake Buchler Instruments, Inc., Saddle Brooke, NJ), with a mixing volume capacity of 60 ml, was used to mix the NaCMC with deionized water at a temperature of 25 °C and a speed of 25 rpm for 5 minutes after reaching steady state. The mixture was sealed into ointment jars, which were kept in a refrigerator for at least a day at 4 °C in order to let the system completely hydrate. The second was a concentrated suspension of a curable silicone polymer (30K cSt) incorporated with 94% by weight of low aspect ratio particles and mixed in a Baker-Perkins 50.8 mm fully-intermeshing corotating twin screw extruder (Fluid II).

An Instron capillary rheometer was used for the characterization of the shear viscosity and the wall slip behavior of the gel system. Experiments were carried out at room temperature using different capillary dies with diameters of 0.03 inch (0.762 mm), 0.0591 inch (1.5 mm) and 0.0984

inch (2.5 mm). The length over diameter (L/D) ratios of the dies were 20, 40 and 60 for each diameter and entrance angles of the dies were  $45^{\circ}$ .

An off line adjustable gap slit die was used in conjunction with the Instron Universal Tester. A cartridge, which can be independently filled by using a hydraulic mechanism and under vacuum, was used to compress the samples under 1500 psi to remove the air bubbles from the sample and obtain a uniform structure. The width of the rectangular slit die was 1.5 in and three different gap openings (0.7 to 1.5 mm) were used during the experiments under ambient condition (~21°C). The barrel was filled with about 4 inches height of material. The temperature and pressure readings of the four transducers, which were equally spaced along (flow direction) the slit, were monitored and recorded using National Instruments hardware and LabView based program. Every condition was repeated at least trice and water content of the samples was measured before and after the experiments and difference was less than 1%.

The parameters of the shear viscosity material functions of the gel and the suspension (Hershel-Bulkley type viscoplastic constitutive equation for the gel and the suspension and a simple powerlaw type shear viscosity expression for the binder of the suspensions).

Type I. Bulk fluid:  $m_0 = 3500 \text{ Pa.s}^n$ , n = 0.336,  $\tau_0 = 1000 \text{ Pa}$ 

Type II. Bulk Fluid:  $m_0 = 10424 \text{ Pa.s}^n$ , n = 0.84,  $\tau_0 = 4300 \text{ Pa}$ 

Binder:  $m_0 = 26.2 \text{ Pa.s}^n$ , n = 1.0;  $\delta_a = 0.63 \text{ }\mu\text{m}$ 

#### **Results and Discussion**

For computational amenability of the governing equations via FEM analysis, the apparent slip layer thickness,  $\delta$ , was assumed to be varying along the axis of flow channel, i.e., the main flow direction, z, concomitant with the decrease of the pressure along the length of the die as a direct consequence of the pressure dependence of the Navier's slip coefficient,  $\beta(P)$ , [5, 6].

$$\delta(P) = \delta_a \left(\frac{P_a}{P + P_a}\right)^{\kappa}$$

where,  $\kappa$  is slip exponent and  $\delta a$  is the nominal slip layer thickness at the ambient pressure Pa. P = P(z) is the bulk pressure of the flow channel transverse to the main flow z-direction:  $P = \frac{1}{A} \iint_{A} p(x, y, z) dx dy$ 

where p=p(x, y, z) is the fluid pressure and A=A(z) is the cross-sectional sectional area.

In order to ascertain the accuracy of solutions from the computer code based on the foregoing analysis and determine the finite element mesh sizes, calculations were carried out for the flow of the two fluids with apparent slip layer of uniform thickness and compared with the available analytical solution of capillary flow of viscoplastic fluids subject to apparent slip at the wall [7]. The uniform thickness slip layer solution corresponds to the case of pressure independent ( $\kappa =$ 

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0.0) slip layer. The numerical solutions matched very closely with those of the analytical solutions [results not shown]. The numerical simulation and experimental results covered the capillary flow using different dies with constant diameter but differing length over diameter ratios and different flow rates for the same capillary die. The comparisons of the numerical simulation results with the experimental data of Numerical simulations along with the experimental results are shown in Figs. 3 and 4 for Fluids I and II, respectively. For the numerical results, simulations were carried out in the following manner: (1) simulations with the no-slip condition, from  $\delta$ =0, i.e., without the apparent slip layer, (2) simulations of pressure independent slip using slip exponent  $\kappa = 0.0$ , that is, with a binder layer of uniform thickness, and (3) simulations of pressure dependent slip with a slip exponent  $\kappa$ .

As may be seen in Fig. 3 and 4, the experimental results are actually bracketed between the pure suspension simulations and the pressure independent slip simulations. Through a series of numerical experiments with a wide range of slip exponent, it was found that for both Type I and II suspensions, a slip exponent value of  $\kappa$ = 0.4 yields results which agree with experimental data within 0.1 % differences. Although the two fluids are very different in nature (hydrogel versus a concentrated suspension) the same value of  $\kappa$ , i.e.,  $\kappa$ =0.4 was able to generate excellent agreement between the experimental and numerical simulation results for both fluids. The basis for such universal behavior and the mechanisms of the apparent wall slip behavior of such complex fluids (although the preliminary considerations suggest that the release of gases appear to be mainly responsible for the pressure dependence of the apparent slip behavior) need to be further elucidated.



Experiment versus numerical simulation: Flow of type I fluid through converging capillary die (D = 0.0591 inch, L/D = 40)

Figure 3: Experiment versus simulation (FEM) with pressure dependent slip condition for capillary flow of Type I fluid.



## Experiment versus numerical simulation: Flow of type II fluid through converging capillary die (D = 0.0675 inch, L/D = 35)

Figure 4: Experiment versus simulation (FEM) with pressure dependent slip condition for capillary flow of Type II fluid.

#### Conclusions

The pressure dependence of the wall slip boundary condition is shown to be one of the major factors affecting the development of flow instabilities that lead to surface and bulk extrudate irregularities. The determination of the pressure dependent wall slip parameters is a challenge and could be addressed by the inverse problem solution starting from the pressure drop versus flow rate relationship of complex fluids in capillary or rectangular slit dies. The comparison of the experimental and simulated capillary flow behavior was very favorable and suggested that there could be a universal parameter describing the pressure dependence of apparent slip behavior.

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## THE ELASTICITY OF POLYMER MELTS DESCRIBED BY THE FIRST NORMAL STRESS DIFFERENCE

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A method is proposed to characterize the elastic behavior of polymer melts, by calculating the first normal stress difference, N1, over an extended shear rate range which experimental measurements cannot cover. The method is predicated on the extensional data calculated from the Cogswell's abrupt contraction flow analysis of capillary data, [1].

These results are compared with experimental data and results obtained with the Laun's rule [2] for obtaining viscometric functions from linear viscoelastic data as well as results calculated using Johnson-Segalman Constitutive Equation [3] and methods proposed for calculating N1 from viscosity data by A. Khalik, et. al. [4, 5] and Wagner [6]. Agreement is acceptable broadening the potential for employing N1 as a characterization technique.

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## MATHEMATICAL MODELING OF OLEFIN POLYMERIZATION WITH MULTIPLE-SITE-TYPE CATALYSTS

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Despite several recent advances on olefin polymerization catalysis[1], most of the industrial polyolefin production still relies on the use of heterogeneous Ziegler-Natta and Phillips catalysts. These catalysts have several types of active sites, each making polymer with different average properties, which complicates parameter estimation and mathematical modeling of olefin polymerization with them.

Our group has developed several mathematical models and parameter estimation approaches to deal with these important commercial catalysts in the past.[2-6] Recently, we developed two new approaches that combine these techniques into integrated parameter estimation methodologies: 1) simultaneous deconvolution of the molecular weight and chemical composition distributions,[7] and 2) simultaneous deconvolution of the molecular weight and comonomer sequence length distributions.[8-9]

In this presentation we will contrast these two approaches and suggest ways they can be used to better understand multiple-site catalysts. We will also propose ways to improve these techniques in future investigations.

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## CHAIN WALKING COPOLYMERIZATION OF ETHYLENE WITH CYCLOPENTENE

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The discovery of Palladium-diimine catalysts by Brookhart et al. in the mid-1990s [1,2] has provided unprecented freedom in controlling the chain microstructures of polyolefins. These late transition metal catalysts have a characteristic chain walking mechanism, and allow one-step synthesis of polethylenes with controllable chain topology [3-5].

In this study, we carried out copolymerization of ethylene with cyclopentene (as the ring-forming comonomer) by chain walking mechanism. Copolymers containing five-membered rings on the polymer backbone at various low contents (up to 7.5 mol%) were synthesized by controlling cyclopentene feed concentration at different ethylene pressure/temperature combinations (1 atm/15 C, 1 atm/25 C, 1 atm/35 C, and 6 atm/25 C) using a Pd-diimine catalyst. The chain microstructure of the polymers were characterized extensively, and the effect of ring incorporation on polymer chain topology studied. We found that cyclopentene was incorporated in the copolymers (~ 77%) mainly in the form of isolated cis-1,3 ring units, along with a small fraction (~7%) in the form of isolated cis-1,2 ring units. Significant linearization of polymer chain topology was achieved with ring incorporation in each copolymer synthesized at 1 atm. The zero-shear viscosity of the polymer melts was significantly enhanced with an increase of ring content despite the decreasing polymer molecular weight. For copolymers synthesized at 6 atm, the effect of ring incorporation on polymer chain topology was negligible or weaker due to their linear chain topology at this polymerization condition. The results obtained in this study demonstrate that effective tuning of polyethylene chain topology from hyperbranched to linear can be conveniently achieved via incorporation of cyclopentene without changing ethylene pressure or polymerization temperature.

This work is based on a recent publication (S. Morgan, Z. Ye, R. Subramanian, W.-J. Wang, and G. Ulibarri, Polymer, 51, 597-605 (2010)), and submitted here for the conference.

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## POLYETHYLENE FOR SHRINK FILM

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One of the most popular applications of polyethylene is the production of shrink films. This film is used for packing beverage bottles of different sizes. In most cases, this film is a blend of three types of polyethylene: low density (LDPE), linear low density (LLDPE) and high density (HDPE).

In order to understand the mechanical, thermal and flow behavior of this kind of films, blends of LDPE/LLDPE/HDPE were prepared according to a design of experiments for mixtures. Mechanical, thermal and flow properties were determined for these blends. Using a statictical analysis, no-lineal correlations were established for the observed results and the composition of the blend.

Results show that behavior of the blend is strongly affected by the composition of the polyethylene and the polymer type. Moreover, DSC results showed that all the blends prepared were heterogeneous. With the obtained results we can predict properties of a given blend.

## USE OF THE TRIFUNCTIONAL CYCLIC INITIATOR, DEKTP, AS THE RADICAL INITIATOR IN THE MODIFICATION OF POLYPROPYLENE IN THE PRESENCE OF DIFFERENT BRANCHING/CROSSLINKING CO-AGENTS

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### Abstract

Homopolypropylene was modified in the molten state using a new cyclic multifunctional peroxide as the initiator, the Diethyl Ketone Triperoxide (DEKTP), in the presence of different branching/crosslinking co-agents: Trimethylolpropane Triacrylate (TM), Trimethylolpropane Triacrylate Propoxylate (TMP), Pentaerythritol Tetraacrylate (PETA) and N'N'-1,3-Phenylene Dimaleimida (FDM). Experiments were carried out in an internal mixer at 180 °C, using two different concentrations of co-agent/initiator; [0.250/0.025] and [0.50/0.05], molar rate= [co-agent]/[initiator] constant equal to 10. The modified PP's were evaluated by GPC, FTIR, DSC, WAXD and the rheological properties were also evaluated. The results showed the presence of branches in the backbone of PP when it was modified with TM and PETA co-agents.

### Introduction

Isotactic Polypropylene (iPP) has become one of the most widely used commercial polymers because it has many desirable and beneficial physical properties such low density, high melting point, chemical resistance and excellent elongation at rupture, among others. These special properties makes iPP useful in different applications such as houseware, pipelines, bags, and it is widely used in processes that include extrusion and injection molding [1]. However, PP is a linear polymer, which has relatively low melt strength and exhibits no strain hardening behavior in the molten state, which is necessary for processes that require High Melt Strength (HMS) as foaming, cast, blown film, blow molding and thermoforming [2]. One of the most effective approaches to achieve the HMS is the branching/crosslinking of PP [3-5] through reactions with a combination of PP-type polyfunctional acrylate monomer and/or maleimide (branching/crosslinking co-agents) in the presence of a peroxidic initiator that accelerates the reactions of grafting and/or branching [6]. The initiators more commonly used for branching PP are mono- and difunctional peroxides [7-9]. Wang et al. [10] prepared branching PP by reactive extrusion using the 2,5-bis(tertbutylperoxy)-2,5-dimethyl hexane as the initiator and pentaerythritol triacrylate as the branching/crosslinking co-agent at different concentrations. The results of the analysis of various techniques showed that at low initiator concentration the chain's degradation is limited yielding branched PP free of gel.

On the other hand, multifunctional initiators with a functionality of three or greater, offer some advantages over mono-and bifunctional initiators during PP modification processes via reactive extrusion, as they can produce star polymers or products with high branching.

Scorah et al. [11] used the tetrafunctional initiator Luperox JWEB50 during homo- and copolymerization of different vinyl monomers where the polymerization rates, molecular properties and the degree of branching showed the following trends: at low temperature the tetrafunctional initiator significantly reduced the Mw, while at high temperature and low concentration of initiator, the Mw increased as a consequence of chain extension reactions and/or branching. Due to the advantages obtained through the use of multifunctional initiators, this work is based on assessing the effect of the multifunctional cyclic initiator Diethyl Ketone Triperoxide (DEKTP) during the modification reactions of the PP in the presence of four different branching/crosslinking co-agents in order to obtain branched PP's

## Experimental

## Materials

The Homopolymer PP supplied by Valtec has a melt-flow index (MFI) of 7.08 g/10 min measured at 2.16 Kg and 230  $^{\circ}$ C. The co-agents were obtained from Aldrich. Diethyl Ketone Triperoxide (DEKTP) was synthesized in a simple and efficient one-step procedure, by the reaction of the respective ketone with hydrogen peroxide as reported by Cerna et. al.[12].

## Melt modification.

For polymer modification reactions, performed with a Brabender plastograph mixer, 42g of PP was introduced into the mixing chamber at 180 °C and 60 rpm. After 6 min, the branching/crosslinking co-agent was added. Finally, after 2 min the initiator DEKTP was also added to the mixing system. The total reaction time was 30 min. Table 1 shows the formulations used and the nomenclature used.

<b>Table 1:</b> Formulations employed in order to modify the PP, R=[C]/[I]=10.					
Nomenclature	Nomenclature System		[Co-agentes] % mol		
PP virgin	Virgin PP (Ziegler-Natta) (Mn= 232 400g/mol)				
PP/D	PP/ DEKTP	0.050			
PP/TMP/D	PP/Trimethylol propane propoxilate triacrylate /DEKTP	0.050	0.50		
PP/TM/D	PP/ Trimethylol propane triacrylate/DEKTP	0.050	0.50		
PP/PETA/D	PP/ Pentaerythritol tetraacrylate /DEKTP	0.050	0.50		
PP/FDM/D	PP/N'-N'-(1,3-Phenylene) dimaliemide/DEKTP	0.050	0.50		

## Measurements

Gel content was determined by Soxhlet extraction in boiling xylene for 24 h, and no significant gel was formed for modified PP's.

The melt-flow properties of the initial and reacted PP's were measured with an MFI tester Dynisco, according to the ASTMD 1238 standard.

GPC measurements were performed in a GPC V200 Alliance Waters. The samples were dissolved in 1,2,3-trichorobenzene and filtered to remove the insoluble fraction.

Thermal behavior of the initial and modified PP's was investigated with a DSC 2920 from TA Instruments. Specimens were heated to 200 °C at a rate of 10 °C/min to eliminate the thermal history and then cooled down to 25 °C at a rate of 10 °C/min under N<sub>2</sub> flow.

X-ray diffraction experiments were performed on a SIMENS D-5000 X-ray diffractometer set at 35 kV and 25 mA with CuK $\alpha$  radiation.

### **Results and Discussion**

Figure 1 shows the preliminar results of torque analysis of the modified PP's where the time at which the co-agent and the initiator were added are indicated by the signals at 6 and 8 min correspond to the aperture of the mixing chamber by a decrease torque values. The torque curve remains without significant changes in the case of virgin PP meanwhile in the case of using the co-agents TM, PETA and FDM, a maximum in the signal can be observed which suggests the presence of crosslinking reactions. As the presence of gels was not observed, the increase in the torque curves was associated to an increase in the system's viscosity as a consequence of the crosslinking reactions in a similar way to that observed by Zhou et al.[13].



Figure 1: Plastograms of modified PP's with R=10 (co-agent/initiator) 0.5/0.05

Table 2: Me	It flow index	x and mol	ecular weights of		
the modified PP 's.					
<b>G</b> (	MFI	м			

System	MFI (g/10 min)	Mw (g/mol)	Mn (g/mol)	PDI
PP virgin	7.08	232 400	80 142	2.89
PP/D	15.28	206 294	49 542	4.16
PP/TMP/D	31.33	181 489	63 236	2.88
PP/TM/D	9.89	289 399	71 430	4.06
PP/PETA/D	9.74	259 115	79 959	3.24
PP/FDM/D	14.05	188 048	65 711	2.86

MFI=Melt Flow Index

PDI=Polydispersity Index

The effect of PP modification on MFI and Mw can be observed from Table 2. The Melt flow index (MFI) values for the modified PP's are higher than the virgin PP associated to chain scission reactions of the PP backbone by the radicals produced by the initiator [13].

In the case of using *TMP* as the co-agent, the MFI values are the highest ones (and the lowest the Mw's) probably due to the 3 propoxilates groups– $[O(CH_2)]_3$  in the structure of the co-agent that produce a better stabilization in the radical produced due to electronic delocalization, decreasing the reactivity of the sites capable of grafting onto the tertiary carbons of the PP backbone [14,15].

In the case of the *TM* co-agent, the Mw increases but the MFI decreases probably as a consequence of the presence of branched/crosslinked polymer. As the gel content is negligible, the probable existence of branching polymer modifies the hydrodynamic volume of the molecule. In comparison with the virgin PP the MFI values are higher; instead the Mw's are higher. This behavior can be attributed to the increase in PDI as a consequence of chain scission and branching, where the species of lower Mn can act as lubricants increasing the MFI [11,13].

When *PETA* is used as the co-agent, the behavior is similar to that presented by *TM*, and the PDI values are lower due to the co-agent tetra-functionality that gives rise to a large crosslinking or

branching density due to a mayor crosslinking capacity of the co-agent, with a minor proportion of scission reactions [10,16].

Finally, the PP's modified with the *FDM* present the lowest values of Mw related to two possible situations: the first one associated to the structure of the co-agent, since maleimide co-agents can stabilized the macroradical product which can react once again with the PP to generate PP•, increasing the  $\beta$ -scission reaction and decreasing the Mw. The second situation involves the stabilization of the macroradical by the co-agent followed by intermolecular coupling between macroradicals and/or PP's macroradical yielding high branched/crosslinked materials which due to the decrease in the hydrodynamic volume present an apparent lower Mw [17].

Taking into account the PP's with better molecular properties (the ones obtained with *TM* and *PETA*), their thermal and crystalline properties were analyzed in order to corroborate the presence of branching into the PP main chain.

In the case of the thermal properties, the modified PP's present a slight higher fusion temperature than the virgin PP (Table 3). With respect to the crystallization temperature (Tc) it is higher in PP/D probably due to the scission that suffer the PP chains, induced by the DEKTP without coagents, that enhance mobility of the molecular chain segments favoring the diffusion and arrangement of macromolecules in the crystal cell, therefore the crystallization temperature rate is higher and crystallization temperature increases [18]. On the other hand, in the presence of coagents (PP/TM/D and PP/PETA/D), Tc is higher than in virgin PP due to the existence of branching or crosslinking units which considerable increase the nucleation density of PP and accelerate the crystallization [19,20].

Table 3: Thermal Properties for the virgin
and modified PP's with TM and PETA

System	Tm (°C)	Tc(°C)
PP	163.71	108.90
PP/D	163.52	112.06
PP/TM/D	165.39	126.38
PP/PETA/D	165.06	124.72



**Figure 2:** Difractograms of PP's modified with R=10 (co-agent/initiator)

Figure 2 shows the diffractograms of PP and PP's modified with TM and PETA. The peak at  $2\theta$ =19.7° corresponds to the (117) plane of the  $\gamma$  crystalline phase and it is related to the presence of some structural defects on the PP backbone, so that this peak is only present when the co-agents were used as a consequence of branched/crosslinked structures [21,22]. The crosslinking/grafting reactions that take place during PP modification could interrupt the isotactic sequence of PP, resulting in the formation of the  $\gamma$ -phase PP crystals. On the other hand, the porcentages of crystallinity (%Xc) obtained in the case of PP/TM/D and PP/PETA/D, are lower than the values for virgin PP due to the presence of these structural defects that prevent the

order of the molecules [23]. These results are in agreement with the ones obtained from the molecular and flow properties.

## Conclusions

During the modification of PP using the multifunctional cyclic initiator DEKTP and different crosslinking co-agents, the systems PP/TM/D and PP/PETA/D were the more efficient during the grafting, scission, branching/crosslinking reactions. The modified PP's obtained with PETA, present a minimum degradation (chain scission) due to the tetra-functionality of the co-agent. The Tc of the modified PP's using TM and PETA were higher than the ones for virgin PP and PP's without co-agents (PP and PP/D), due to the presence of branching onto the main PP backbone. In the modified PP's with TM and PETA, the  $\gamma$  crystalline form was detected and together with the % crystallinity values, the presence of structural defects in the PP backbone was evidenced.

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## DEVELOPMENT POTENTIAL FOR THE MEXICAN POLYOLEFINS INDUSTRY POSSIBLE ROLE OF THE FEDERAL GOVERNMENT AND GOVERNMENT OWNED COMPANIES

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The Mexican Petrochemicals Industry was born under a highly protectionist economy which had to be essentially dismantled in 1986-1987 as a basic requirement to be able to negotiate the North American Free Trade Agreement (NAFTA) with the US and Canada which was started in 1991. Most manufacturing plants until 1980 were downsized against international benchmarks, resulting in an intrinsic competitive disadvantage on economies of scale. This and other competitive disadvantages were compensated through tariff and non-tariff barriers and from 1978 projects were also supported by subsidies established as a discount up to 30% on prices of raw materials and energy provided by Government owned companies (essentially Petroleos Mexicanos - PEMEX).

This artificial competitive structure was questioned and eliminated by the end of 1987. Furthermore, during the NAFTA negotiation, a separate chapter was considered including specific provisions for pricing raw materials and other commercial disciplines which should be considered by Government owned companies in order to prevent the Mexican Government and its Agencies to relapse into subsidy practices. Parallel to these changes, the NAFTA also redefined the division limits for public and private activities on Petrochemical related activities; the public or "basic" activities were reduced to the production of pure molecules typically present in natural gas and its liquids.

A major problem arose as pricing for some of these materials (like ethane) could not be easily resolved by the standard mechanism of indexing it to representative published prices in relevant international markets. More than 15 years were elapsed since the coming into force of the NAFTA in 1994 in order to put in place an alternative commercially based pricing mechanism which would comply with the NAFTA provisions. Fortunately, this has already happened and this action is allowing the development on a very significant project for transforming ethane to ethylene and from there into polyethylenes.

In this presentation we briefly explore alternative scenarios that could follow after this significant step ahead, including the most important opportunities and restrictions that we could face in their development.

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## PREPARATION OF POLYETHYLENES BEARING A FUNCTIONAL CHAIN END AND THEIR USE FOR THE DESIGN OF ORIGINAL POLYETHYLENE BASED MATERIALS

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The incorporation of functional groups at the end of polyolefin chains offers an opportunity to prepare polyolefin building blocks. The latter can be used to construct polymer architectures based on polyolefin with many desirable properties.<sup>1</sup>

Despite their great success, there are some inherent shortfalls in polyolefins materials such as the lack of reactivity that prevent their wider usage in many areas. Incorporating functional groups into polyolefins has been the focus of many studies however, the challenge remains to reach chemistries that are selective and quantitative and that allow the introduction of versatile reactive groups.

For that purpose, the reactivity of carbon-metal bond formed during a catalytic olefin polymerization process is particularly appealing. The possibility of taking advantage of this reactivity has been enhanced by the discovery of original features in specific catalytic systems where the growing polymer chain is rapidly and reversibly transfer between the active centre and a main group metal.<sup>2</sup> Main group organometallic compounds used in these systems indeed act as reversible chain transfer agent (CTA) according to a mechanism of degenerative chain transfer. Making the most of this particular concept of Coordinative Chain Transfer Polymerization, we prepared dipolyethylenylmagnesium compounds (PE-Mg-PE) by ethylene polymerization using  $(C_5Me_5)_2NdCl_2Li(OEt_2)_2$  complex in combination with n-butyloctylmagnesium (BOMg) according to original works of Pelletier et al.<sup>3</sup>

We have shown that the nucleophilicity of the carbon moiety in PE-Mg-PE can favor the introduction of various functions at the end of PE.<sup>4</sup> As narrowly distributed (PDI<1.2) short alkyl chains to crystalline PE (up to 5000 g.mol<sup>-1</sup>) can be reached using this catalytic system, we wish to report here on their use for further modification, reaction with organic and inorganic materials or incorporation into more complex architectures.

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### POLYMERIZATION OF 1,3-DIENE MONOMER WITH SEVERAL CATALYTYC SYSTEMS BASED ON NEODYMIUM OR BUTYL LITHIUM IN THE PRESENCE OF IONIC LIQUIDS

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#### Abstract

The anionic and Ziegler-Natta polymerization of 1,3-butadiene in cyclohexane with n-BuLi and NdV/TIBA/DEAC separately as catalytic system in the presence of ionic liquids (LIs) were carry out. The presence of ionic liquids leads to a decrease in the reaction exothermal and in both cases there is a decrease in the molecular weight distribution (MWD) using LIs.

#### Introduction

Today it is widely known that in anionic polymerization, the versatility of alkyl lithium-based initiator especially *n*-Butyl Lithium (n-BuLi) yields polybutadiene (PB) with a broad scope of molecular structure of controlled dimension. On the other hand, the neodymium (Nd)-based homogenous Ziegler-Natta catalytic system, allows PB with the highest *cis*-1,4-content [1]. By means of these catalysts PB with a *cis*-1,4-content up 98 % can be obtained. A typical tertiary catalytic system comprises: Neodymium salt/alkylating co-catalyst/chlorinating agent. For example: neodymium versatate (NdV)/triisobutyl aluminum (TIBA)/diethylaluminum chloride (DEAC). In both cases anionic and Ziegler-Natta polymerizations using solvents, the kinetic of polymerization, molecular weight distribution (MWD) and the stereochemistry of 1,3-diene insertion depends on several parameters like polymerization temperature, type of active species, monomer concentrations and more particularly the presence of Lewis base and acid additives for anionic polymerization [2]; or type of Neodymium salt, co-catalyst, chlorinating agent and preparation of the catalytic system (aged or "*in situ*") for Ziegler-Natta systems [3,4,5].

In recent years ionic liquids (LIs) have been extensively investigated for replacing solvents in clean syntheses for a variety of chemical reactions. In anionic polymerization there are few reports detailing the synthesis of polymers in the presence of LIs [6,7,8]. In the case of niobium-based catalysts there is a report on butadiene polymerization using LIs as solvent [9]. For other kind of monomers a detailed document about the polymerization of methyl methacrylate (MMA) and St (styrene) using the catalytic system NdV/TIBA is reported by Xion and Shen [10]. However until our knowledge there are no reports about the use of LIs in anionic or Ziegler-Natta polymerizations using n-BuLi and NdV respectively as catalysts for butadiene polymerization.

In this communication we report the anionic and Ziegler-Natta polymerization of 1,3-butadiene using mixtures of cyclohexane and several LIs s solvent. The results are compared with polymerizations carry out using only cyclohexane under similar polymerization conditions.

#### Experimental

#### Chemicals

All manipulations were carried out in inert atmosphere using dual vacuum argon line and standard Schlenk techniques. Cyclohexane was distilled from sodium under argon before use, and was handled and stored under inert atmosphere. Before using, the ionic liquids 1-Butyl-3-ethylimidazolium hexafluorophosphate [BMIM][PF<sub>6</sub>], 1-Butyl-3-ethylimidazolium methyl sulfate [BMIM][MeSO<sub>4</sub>] and 1-ethyl-3-ethylimidazolium chloride [BMIM][Cl] from Aldrich,

were dried under vacuum. For anionic polymerizations 1.6 M of *n*-BuLi/hexane solution (Aldrich) was used as supplied. The chemicals for Ziegler-Natta polymerization, 1.0 M of TIBA/hexane solution was prepared and 1.0 M of diethyl aluminum chloride (DEAC)/hexane solution was used as supplied, both from Aldrih. 40 wt %. Neodymium versatate (NdV<sub>3</sub>)/hexane solution from RHODIA was used as supplied. Butadiene from Praxair was purified by passing through activated molecular sieve 4A and alumina.

#### **Polymerization reactions**

Polymerizations were carried out in a 1 L stainless steel Parr reactor. Separately cyclohexane and ionic liquid were introduced in the reactor under argon atmosphere. The 1,3-diene monomer was added using a 50 mL stainless steel container. The reactor was heated to 60  $^{\circ}$ C under agitation. Finally, the catalytic system was fed in the reactor using a syringe (n-BuLi for anionic polymerizations and NdV3/TIBA/DEAC aged 5 min at room temperature for Ziegler-Natta polymerizations). All reactions were terminated by adding acidified methanol, the polymer was precipitated and washed with methanol and filtered in order to separate the ILs. The resulting polymer was dried under vacuum until constant weight was reached. The polymer was characterized by gel permeation chromatography (GPC) to obtain their molar mass and the molecular weight distribution.

#### **Results and discussions**

Tables 1 and 2 summarize the conditions and results of the anionic and Ziegler-Natta polymerizations respectively, using different ionic liquids.

**Table 1.** Anionic polymerizations of 1,3-butadiene in cyclohexane with n-BuLi as initiator using Ionic Liquids.

Run	Ionic Liquid (mol)	$T_{initial}$ ( <sup>0</sup> C)	$\Delta T (^{0}C)$	$M_{ m n,cal}$	$M_{\rm n,obs}$	$M_{ m w}/M_{ m n}$
A-1	-	62	19	14900	35600	1.29
A-2	[BMIM][MeSO <sub>4</sub> ]:0.0120	63	14	14900	25600	1.23
A-3	[BMIM][MeSO <sub>4</sub> ]:0.0240	67	18	13600	25300	1.18
A-4	[EMIM][Cl]:0.0185	63	15	13750	18000	1.20
A-5	[EMIM][C1]:0.0370	64	15	15500	25400	1.19

Solvent: 1.388 mol; n-BuLi: 0.0016 mol; Monomer: A-1: 0.441 mol; A-2: 0.441 mol; A-3: 0.4030 mol; A-4: 0.4067 mol; A-5: 0.4584 mol; polymerization time: 120 min. In all polymerization the conversion reached was 100 %.

		,	· ·		
Run	Ionic liquid (mol)	$T_{initial} (^{0}C)$	$\Delta T (^{0}C)$	$M_{ m n}$	$M_{ m w}/M_{ m n}$
ZN-1	-	57	20.1	57400	8.25
ZN-2	[BMIM][PF <sub>6</sub> ]:0.0194	61	16.3	88000	5.48
ZN-3	[BMIM][PF <sub>6</sub> ]:0.0291	60.5	18.9	67200	3.91
ZN-4	[BMIM][PF <sub>6</sub> ]:0.0388	62.7	18.5	112000	3.67

Solvent: 2.77 mol; Catalytic system: NdV<sub>3</sub>/TIBA/DEAC aged 5 min at room temperature; Monomer: ZN-1: 0.399 mol; 2: 0.482 mol; ZN-3: 0.447 mol; ZN-4: 0.447 mol; polymerization time: 180 min.

When the Anionic and Ziegler-Natta polymerizations of 1, 3-butadiene was carried out in the presence of ionic liquid a decrease in the reaction exotherm is presented (see Figs. 1 and 2). The decrease is more pronounced in the anionic polymerization because the solvent/ionic liquid solvent ratio is lower. This behavior is attributed to the fact that ionic liquids can be used as moderators in exothermic polymerization reactions due to its thermal stability [11]: In all cases, in the anionic polymerization the MWD decrease when the ionic liquid is added to the reaction medium (see Table 2). These results suggest that the ionic liquid promotes rapid initiation and prevents an increase in the polydispersity. And they may be acting as scavengers reducing the amount of killers in the reaction medium.

In the Ziegler-Natta polymerizations the presence of ionic liquid could promote the production of more stable and homogeneous active sites giving high molecular weight polymers and narrower molecular weight distributions. In this case the polymerization of 1,3-butadiene could proceed with a lower proportion of chain transfer events with ionic liquid presence. In other words, the performance of the catalytic system is depending on the reaction medium (solvent). Fig. 2 shows the behavior of the conversion as a function of the reaction time. We can see that by adding different amounts of ionic liquid to the reaction medium, the conversion achieved is lower. In this case, the catalytic system may have been deactivated by the attacking of the ionic liquid [BMIM][PF<sub>6</sub>] species.



**Figure 1.** Evolution of temperature as a function of time in anionic polymerizations: A-1: 0 mL LIs; A-2: 2.5 mL [BMIM][MeSO<sub>4</sub>]; A-3: 5 mL [BMIM][MeSO<sub>4</sub>]; A-4: 2.5 mL [BMIM][Cl]; A-5: 5 mL [BMIM][Cl]



**Figure 2.** Evolution of yield as a function of time in Ziegler-Natta polymerizations: ZN-1: 0 mL LIs; ZN-2: 4 mL [BMIM][PF<sub>6</sub>]; ZN-3: 6 mL [BMIM][ PF<sub>6</sub>]; ZN-3: 8 mL [BMIM][ PF<sub>6</sub>]

#### Conclusions

The addition of ionic liquid in the Ziegler-Natta polymerizations of 1,3 butadiene, using catalytic systems based on neodymium, promotes the production of high molecular weights and decreases the polydispersity. In the anionic polymerization of the same monomer using n-BuLi, the presence of ionic liquids decreases the polydispersity. In both types of polymerizations the presence of ionic liquids diminished the reaction exotherms.

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## KINETIC MODELING OF THE SPINODAL DECOMPOSITION OF DILUTE POLYOLEFIN SOLUTIONS

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Liquid-liquid separations of polymer solutions are of interest in a number of industrial applications. Among these are the temperature and pressure induced phase separations utilized in polyolefin membrane processes and in polymer concentrators used in solution polymerization processes. In both of these examples, the kinetics of spinodal decomposition are as important as the phase equilibria. The evolution of droplet size, the time to phase inversion, or the equilibrium phase volumes are in many ways the controlling aspects of these processes. To capture the kinetics of these phase separations a first-principles model has been developed which describes the mass transfer during spinodal decomposition under a thermodynamic driving force. The model development and validation with literature data is presented.

## MICROCELLULAR AGAVE FIBRE-HIGH DENSITY POLYETHYLENE COMPOSITES PRODUCED BY INJECTION MOLDING

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#### Abstract

In this study, high density polyethylene-agave fibre composites were foamed using a chemical foaming agent (azodicarbonamide). The samples were produced by injection molding with the objective to produce symmetric and asymmetric structures. To this end, the temperatures of both parts of the mold were independently controlled. From the samples produced, density measurements were performed. As expected, the density of the composites increased with fibre content and decreased with foaming agent content. For mechanical properties characterization, tensile tests were carried out on foamed and unfoamed composites. Young's modulus increased with agave content, but strain at break decreased with increasing agave content. Moreover, Young's modulus and strain at break decreased with increasing foaming agent content. Actually, the microcellular foams were found to have a different tensile behavior than their natural fiber-reinforced microcellular foams counterparts, especially in terms of break-up. Considering the experimental results obtained, natural fiber-reinforced microcellular foams present interesting properties for different technical applications.

#### Introduction

Polymer-natural fibre composites are a relatively new group of environmental friendly materials. Natural fibre reinforced plastics offer several advantages over neat polymers in terms of cost and mechanical properties. This kind of composite is extensively applied for interior and exterior furniture, material handling, packaging, building applications and in the automobile industry. In our group, recent studies highlighted the morphology and mechanical properties of wood fibre-reinforced microcellular foams [1-3]. However, the properties of these materials have not been fully explored and described especially with respect to natural fibre-reinforced microcellular foams with different composite structures.

#### Experimental Material

The polymer matrix was high-density polyethylene (HDPE) grade 60120 supplied by Pemex (Mexico) with a melting temperature of 124°C, a melt index of 12 g/10 min and a density of 962 kg/m<sup>3</sup>. The natural fibre was *Agave Tequilana Weber var. Azul* supplied by a local tequila refinery. As a first step, no coupling agent was used in this study. The chemical blowing agent (CBA) used for foaming was a modified grade of azodicarbonamide from Sigma Aldrich (St-Louis, MO, USA) as a yellow-orange powder. Its decomposition temperature is about 170°C producing 220 cm<sup>3</sup> of gas per gram of CBA.

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#### Sample production

First, to eliminate the extractives in the agave fibres, they were washed three times with water at room temperature. Then, the fibres were dried and milled in a Pulvek Plastic Siemens mill in which a range of particle sizes were obtained. Finally, in a ROTAP automatic siever, particle sizes of 255  $\mu$ m with a L/D ratio of 1.75 were obtained.

Second, the agave fibres were dried at 80°C overnight in order to minimize the amount of volatiles (water). Then, compounding the polymer and agave fibres was done for fibre concentrations of 0, 5, 10 and 20% weight in a twin-screw extruder (Leistritz model Micro 27 GL/GG 32D). The extruder has 27 mm diameter co-rotating screws and the temperature profile was set between 160 and 180°C from the feeder to three circular dies (2 mm in diameter each) with a constant screw speed of 80 rpm. Then, the extruded compound was pelletized and dried at 80°C overnight.

Finally, the compounds were injection molded in a Nissei Press (ES-1000) using a rectangular mold of 80 x 40 x 2.5 mm<sup>3</sup>. To obtain foamed composites 1% of CBA was blended with the compounds. Different temperatures were applied to both parts of the mold. For symmetric structures (same temperature on both sides), six temperatures were chosen in the range of 30-80°C, with steps of 10°C. For asymmetric structures, the fix part of the mold was kept at 30°C, while the moving part was controlled in the range 30-80°C, with steps of 10°C.

## Density

Sample density was measured using a gas (nitrogen) pycnometer model Ultrapyc 1200e (Quantachrome Instruments, Boynton Beach, Florida, USA). The values reported are the average of at least five measurements.

### **Tensile properties**

Determination of the tensile properties like Young's modulus (*E*) and elongation at break ( $\varepsilon_b$ ), was performed on an Instron universal tester model 5565 (Instron, Norwood, Massachusetts, USA) with a 500 N load cell. Dog bone samples were cut directly in the molded plates according to ASTM D638 (type V). Because of the inherent fragility of these composites under tensile stress, the measurements were performed at a low speed of 2 mm/min and room temperature. The values reported are the average of at least five measurements.

## **Results and Discussion**

### Density

Figure 1 shows the density of symmetric and asymmetric composites. According to HDPE and agave fibres individual densities, the unfoamed composites' density increases linearly as fibre concentration increases. Foamed composites produced with 1% CBA were also molded so as to insure that they have uniform densities in order to compare the effect of cellular morphology on sample properties. In fact, all samples were molded in such a way as to maintain comparable polymer fractions. Since wood cannot be foamed, increasing the amount of wood in the sample will necessarily decrease the overall void fraction. As shown in Figure 1, decreasing void fraction with increasing wood content was therefore unavoidable [1]. The void fraction is represented by the difference between the unfoamed composites and foamed composites densities. Similar results were obtained for all the temperature couples applied on the mold. With symmetric mold temperature (30°C), the void fraction decreases from 27% to 4% when fibre content increased from 0% to 20%.

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However, the analysis of void fraction represents the sum of the gas cells (bubbles) part and the voids created at the fibre-matrix interface due to bad adhesion. In fact, all samples were molded without coupling agent addition. Therefore increasing fibre content in the sample increases the total fibre-matrix interface where voids can accumulate.



Figure 1: Molded part density for a) symmetric and b) asymmetric composites and foams.

#### **Tensile properties**

Young's modulus is presented and compared in Figures 2 and 3. The presence of void in the material increases brittleness. In accordance with a previous study [2], tensile modulus of the neat polymer foamed samples is lower than those of unfoamed samples since less material is available to sustain the applied stress [4]. The presence of void in the material increases the brittleness. However, this effect is almost inexistent when the amount of fibre increases in the material. For this reason, the difference in Young's modulus between the unfoamed and foamed composites molded with symmetric temperature (30°C) decreases from 31% to 6% when fibre content increase from 0% to 5%. Similar to previous studies with hemp/polypropylene (PP) composites [5], Young's modulus increased by 33% and 80% with increasing agave content from 0% to 20% for unfoamed and foamed composites, respectively. Figures 2 and 3 also show that the modulus did not varied substantially with changes in mold temperature.

Elongation at break (complete failure) was also studied and is reported in Figures 4 and 5 where low values are associated with fragile samples. First, the elongation at break highly decreases with the addition of CBA and fibres. For example, increasing CBA from 0% to 1% decreases the elongation at break by 86% and 25%, respectively with respect to the neat polymer and unfoamed composite at 20% agave content, and so independently of the symmetric or asymmetric mold temperature applied. Furthermore, according to Gosselin et al. [2], Figures 4 and 5 show that elongation at break is the only mechanical property to vary significantly with mold temperature: elongation at break decreases with increasing mold temperature. For example, when increasing the mold temperature from 30°C to 80°C (symmetric mold temperature), the elongation at break decreases by 65% for foamed composites, while increasing the mold temperature difference from 0°C to 50°C (asymmetric mold temperature difference), elongation at break decreases by 35% for foamed composites. According to Thomas et al. [6], plastic deformation is governed by the
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amorphous phase in semi-crystalline polymers. As previously mentioned, higher mold temperatures can induce higher crystallinity levels which are associated with fragile behaviors [2]. Further investigation would be needed to confirm this assumption.



Figure 2: Young's modulus of a) unfoamed and b) foamed composites molded with symmetric temperatures.



Figure 3: Young's modulus of a) unfoamed and b) foamed composites molded with asymmetric temperatures.



Figure 4: Elongation at break of a) unfoamed and b) foamed composites molded with symmetric temperatures.



Figure 5: Elongation at break of a) unfoamed and b) foamed composites molded with asymmetric temperatures.

#### Conclusion

In this study, foamed and unfoamed natural fibre composites based on HDPE and agave fibres were molded by injection. The effect of agave fibres, blowing agent and mold temperature were investigated to determine the effect of processing conditions and composition on the final morphology (density) and tensile properties. Density analysis shows that the void fraction was relatively unaffected by mold temperature. Analysis of the tensile properties shows that Young's modulus increased with fibre content, decreased with CBA addition, but was mostly unaffected by mold temperature, in the range of parameters studied, was found to have a relatively small effect on the elongation at break. For future work, the analysis of the cell morphology (size and distribution) and skin thickness are in progress to evaluate the relative amount of void produced by the gas bubbles (foam cells) and the voids present at the fibre-matrix interface. Also, other mechanical properties will be investigated (flexion, torsion, impact).

#### Acknowledgements

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## CATALYTIC HOMOGENEOUS HYDROGENATION OF LINEAR STYRENE-BUTADIENE POLYMER USING NI/LI AND TI/LI CATALYSTS

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## Abstract

This report deals with the production and characterization of poly(styrene-*b*-[(butadiene)<sub>n-x</sub>-(ethylene-co-butylene)<sub>x</sub>]*b*), SBEB, which was produced by homogeneous catalytic hydrogenation of commercial polymer: Solprene 1205 poly(styrene-*b*-butadiene-*b*), SB. Two different catalysts were used, one prepared with nickel (II) bis-acetylacetonate and the other one with bis ( $\eta_5$ -cyclopentadienyl)-titanium(IV) dichloride, both having n-butyllithium as co-catalyst. Characterization of neat and hydrogenated polymers was accomplished by gel permeation chromatography, proton nuclear magnetic resonance spectroscopy, and differential scanning calorimetry. Results indicate that Ti/Li catalyst is more active, since similar hydrogenation level is reach with smaller amount of catalyst; and with both Ni/Li and Ti/Li catalyst the saturation rate of 1,2-vynil is higher than those of 1,4-trans and 1,4-cis polybutadiene units. In regard to the polymer's properties, results indicate that increasing the saturation of the butadiene isomers result in an increase of the mechanical resistance of the polymer and that hydrogenated polymers with a saturation degree higher than 30% exhibit crystallinity.

## Introducción

Los polímeros de dienos conjugados y vinilaromáticos se utilizan ampliamente en la industria como elastómeros [1-3]. Estos polímeros contienen dobles enlaces en su cadena cuya presencia ocasiona una estabilidad térmica limitada y una pobre resistencia al oxígeno y ozono atmosféricos. Por ello, el uso de estos polímeros en aplicaciones que exigen su exposición al medio ambiente es limitado.

Esta deficiencia en resistencia puede ser mejorada notablemente mediante la hidrogenación total o parcial de los dobles enlaces presentes en estos polímeros. Se han propuesto numerosos métodos para lograrlo, tanto catalíticos (homogéneos y heterogéneos) como no catalíticos.

Se han reportado estudios sobre la hidrogenación no catalítica de polímeros [4,5] que indican que es posible obtener un considerable grado de saturación; sin embargo también ocurren reacciones indeseables de degradación y ciclización, dando como resultado materiales con propiedades físicas y mecánicas inferiores.

Los catalizadores heterogéneos generalmente poseen una actividad más baja que los catalizadores homogéneos, por lo que la hidrogenación debe llevarse a cabo a elevada temperatura y alta presión, lo que puede producir que el polímero sufra degradación o gelación, además de que se requieren grandes cantidades de catalizador y el proceso puede presentar problemas de transferencia de masa y calor.

Los catalizadores homogéneos generalmente trabajan bien a temperaturas y presiones moderadas, y la cantidad de catalizador necesaria para lograr una hidrogenación efectiva es menor. Sin embargo, la eliminación de los restos catalíticos de los productos de reacción, que es necesaria porque estos restos afectan desfavorablemente a la estabilidad de los polímeros hidrogenados, es una etapa complicada y costosa.

Este trabajo reporta la hidrogenación de un copolímero estireno-butadieno mediante el uso de dos catalizadores homogéneos diferentes, uno preparado con bis-acetilacetonato de níquel (II)/n-butillitio y el otro con bis-( $\eta_5$ -ciclopentadienil)-titanio (IV)/n-butillitio.

## Experimental

### Materiales

El polímero comercial (Solprene 1205), ciclohexano y n-butillitio fueron donaciones de Dynasol Elastómeros de México; bis-acetilacetonato de níquel (II), bis-( $\eta_5$ -ciclopentadienil)-titanio (IV), tolueno, and tetrahidrofurano fueron adquiridos de Sigma-Aldrich.

### Preparación del catalizador

#### Catalizador Ni/Li

Se pesa la cantidad deseada de bis-acetilacetonato de níquel (II) bajo atmósfera de nitrógeno, después se disuelve en tetrahidrofurano previamente purificado, posteriormente se agregó lentamente n-butillitio hasta alcanzar la relación molar deseada de Ni/Li; inicialmente la solución presentaba un color verde claro y conforme el cocatalizador fue agregado la solución cambió a un color café obscuro.

### Catalizador Ti/Li

Básicamente los dos catalizadores se preparan de la misma forma con la diferencia de que el titanoceno se disuelve en tolueno purificado; esta solución presenta un color rojo que cambia a café obscuro cuando se le agrega n-butillitio.

#### Hidrogenación

La hidrogenación se llevó a cabo en un reactor de vidrio de 1 litro. El proceso para la hidrogenación del polímero consiste en tres pasos consecutivos: primero se disuelve el polímero en ciclohexano purificado, se agita y calienta hasta alcanzar la temperatura deseada (70°C); posteriormente se eliminan las impurezas que desactivan al catalizador mediante una titulación colorimétrica [6]; finalmente se inyecta al reactor la cantidad deseada de catalizador el cual es preparado justo antes de ser adicionado y se presuriza con hidrógeno a 40 psi, manteniéndose constante esta presión a lo largo de la hidrogenación. Se toman muestras a diferentes tiempos de reacción, se desactivan, precipitan con etanol y se secan a vacio para su posterior caracterización.

#### Caracterización

El peso molecular de los polímeros fue determinado por cromatografía de permeación en gel (GPC). La microestructura del polímero fue determinada por resonancia magnética de protón (<sup>1</sup>H-RMN). La temperatura de transición vítrea (Tg) fue medida en un calorímetro diferencial de barrido (DSC).

#### **Resultados y Discusión**

En la Tabla 1 se presentan las características moleculares del polímero Solprene 1205, el cual fue hidrogenado con alguno de los dos catalizadores Ni/Li o Ti/Li bajo condiciones similares resumidas en la Tabla 2. Las condiciones de hidrogenación para ambos sistemas catalíticos, Ni/Li y Ti/Li fueron tomadas de estudios previos [7, 8] y [9] respectivamente.

Propiedad	SB
Arquitectura de la cadena	lineal
Composición (% peso estireno) <sup>a</sup>	25
Peso molecular (g/mol) <sup>b</sup>	90,000
Polidispersidad	1.02
Composición isomérica del polibutadieno <sup>a</sup>	
(% 1,2-vinil)	9
(% 1,4-trans y -cis)	91
Temperatura de transición vítrea, Tg (°C) <sup>c</sup>	-86
Cristalinidad (%) <sup>c</sup>	amorfo

Tabla 1. Propiedades del SB (Solprene 1205) usado en la preparación del SBEB.

<sup>a</sup>Estimado de datos de <sup>1</sup>H-RMN de acuerdo a Sardelis, et al.[10]; <sup>b</sup>Medido por GPC usando estándares de poliestireno; <sup>c</sup>Determinado del análisis de DSC.

Tabla 2. Condiciones de reacción para am	ibos sistemas catalíticos
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	Metal/polímero (mmol / 100 g polímero)	Li/metal (mol/mol)	Temperatura	Presión
Ni	2.5	3	70	40
Ti	0.5	4	70	45

El polímero precursor, Solprene 1205, fue hidrogenado mediante cada catalizador, Ni/Li o Ti/Li, muestras de ellos tomadas a diferentes tiempos fueron analizadas para estudiar la evolución del proceso de hidrogenación. Los resultados se muestran en la Figura 1, en la cual el porcentaje de saturación global, la saturación de los tres isómeros del butadieno (calculada de <sup>1</sup>H-RMN), están presentados como una función del tiempo.



Figura 1. Hidrogenación de Solprene 1205 mediante los catalizadores de Ni/Li y Ti/Li. Ti/pol=0.5g/100g pol, Ni/pol=2.5g/100g pol.

Estos resultados indican que la composición de estos dos sistemas catalíticos presenta similares capacidades para saturar los isómeros del polibutadieno, ya que los perfiles de saturación (como una función del tiempo de reacción) son semejantes para ambos polímeros; en

aproximadamente 60 minutos se obtiene una saturación de entre 80-90%. Sin embargo, la cantidad del catalizador de Ti/Li usado en esta reacción fue más pequeña que la del catalizador de Ni/Li por lo que podemos considerar que el catalizador de Ti/Li tiene una capacidad más alta para saturar los dobles enlaces del bloque de butadieno.



Figura 2. Hidrogenación de Solprene 1205 con Ni/Li (izquierda) and Ti/Li (derecha). El porcentaje de saturación de los isómeros 1,2-vinil y 1,4-trans del polibutadieno fueron calculados del análisis de FTIR como función del tiempo de reacción (t, min).

Estos resultados confirman que en el inicio del proceso (t<20 min.) la rapidez de saturación de las unidades 1,2-vinil es más alta que la de las unidades 1,4-tras, indicando que la estereoselectividad de las unidades 1,2-vinil es superior. Después de alrededor de una hora el 90% de las unidades 1,2-vinil han sido saturadas en comparación con el 70% de las unidades 1,4-tras.

Muestra	Mn (g/gmol)	PD (Mn/Mw)	1,2-Vinil (%)	1,4-Trans (%)	Tg pB-b	Cristalinidad %	DSC
1205	90,000	1.02	-	-	-86	-	
1205H			84	15	-16	7.6	
1205HH	93,000	1.03	92	66	21	14.8	

Tabla 3. Características del poli(estireno-b[(butadieno)<sub>1-x</sub>-(etileno-co-butileno)<sub>x</sub>]-b), SBEB, producido por la hidrogenación de Solprene 1205.

Estos resultados revelan que la saturación parcial del pB-b produce un incremento en la temperatura de transición vítrea de la parte elastomérica del polímero, además de que el Solprene 1205 (SB) es amorfo mientras que el SBEB con un relativamente alto porcentaje de saturación de los isómeros del pB-b (>20%) es parcialmente cristalino.

De los resultados de GPC vemos que la hidrogenación provoca un ligero aumento en el peso molecular promedio que es atribuido a la adición de hidrógeno al polímero y dado que la polidispersidad presenta cambios marginales, es posible aseverar que la hidrogenación no produce ruptura de las cadenas o entrecruzamiento de las mismas.

### Conclusiones

Los dos sistemas catalíticos presentan capacidades similares para la saturación de los isómeros del polibutadieno; sin embargo, debido a que la cantidad de catalizador de Ti/Li fue menor que la de catalizador de Ni/Li se considera que el catalizador de Ti/Li tiene una mayor capacidad para

saturar los dobles enlaces carbono-carbono del pB-b.

Se confirmó que la rapidez de saturación de las unidades 1,2-vinil es mayor que la de las unidades 1,4-trans del polibutadieno.

En general, el análisis de GPC de los polímeros precursores así como el de los polímeros hidrogenados revela que para las condiciones experimentales utilizadas (composición del catalizador, temperatura y presión) el proceso de hidrogenación con ambos catalizadores (Ni/Li y Ti/Li) no afecta la distribución de pesos moleculares del polímero.

Los resultados de DSC indican que el Solprene 1205 (SB) es amorfo mientras que los SBEB con un relativamente alto porcentaje de saturación de los isómeros del pB-b (>20%) son parcialmente cristalinos; así como la temperatura de transición vítrea de la parte elastomérica del polímero aumenta conforme la saturación de los isómeros del polibutadieno es mayor y por lo tanto la resistencia termo-mecánica del polímero es mejor.

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## DISTRIBUTED POLYMERIC SENSOR WITH FIBER OPTIC FOR OIL CRUDE LEAK DETECTION.

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## Abstract

To take advance of the properties of the cracking catalyst in the distributed hydrocarbons sensor surface for detect and locate leaks of light hydrocarbons, gives a new sensor that can response to the oil crude, increase the applications to the original sensor. Being that the most of the detection and locate systems of hydrocarbons leaks don't are focused to the high viscosity liquids neither to the dirty fluids due the oil crude have many compounds, resulting an area of opportunity.

## Introduction

For several years, CIMAV and other international institutions has been designed distributed sensors based on micro bends produced in a fiber optic within a polymer cable (1, 2). These micro curves are generated by the expansion of the cable while the presence of a hydrocarbon, from the absorption of a leaky pipe or tubing. The sensor geometry is such that this expansion produces several local micro fiber curves as described in reference (1), which allows detect and locate the leak. However, the modus operandi of these distributed sensors for hydrocarbons, either optical or electrical, its application to crude oil is difficult due to two aspects, the high viscosity, which hinders their absorption by the polymer wire, and the variety of chemicals of the crude oil. This provides a great challenge for developing distributed sensors to provide security for storage and transportation of crude oil, this research provides an alternative to this problem.

## Experimental

The used sensor is made by a hydrocarbon absorbent polymer, and an optical fiber setting in an eccentrically position. Also the sensor has a helical copper wire that fix a nylon strip in the bottom of the sensor; that nylon strip gives to this sensor mechanical reinforcement, and also makes that the force of the swelling goes up, affecting the curvature of the optical fiber while the sensor is in contact with the hydrocarbon.

We added a cracking hydrocarbure catalyze in the surface of the sensor (Co & Mo), so when it enter In contact with the oil crude, it tends to hold the heavy hydrocarbures, cracking a portion of them and disperse them in the surface of the absorbent polymer to make the swelling effect.

## Develop of the sensor

The active part of the sensor is a absorbent polymer based in polybutadiene whit processing additives, like stearic acid, calcium stearate, naftenic oil, dicumil peroxide as cross linking reagent and black carbon as colorant, this compounds was mixed in a plasticorder Brabender and the resulting material was given shape in a extruder whit a round die of 5 mm of diameter.

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With the filament obtained from the extrusion process, this one have a cross linking process in a circular oven at 175°C in two parts of 3.6 minutes, where the middle of two steps are used to cover the sensor surface with the catalyst dust, this steep in the process it's for utilize the adherent surface of the sensor at 175°C and before the cross linking finish; With the filament cross likened and the catalyst added, makes a longitudinal spline whit a circular tool, whit a abrasive cut disk, this spline contains the optical fiber kind GIG625 multimodal, holding by helicoidally winding of metallic wire and this one hold a Nylon band in the button of the sensor and works as mechanic reinforcement and this is the oil crude sensor test section, every parts of the sensor are shown in the figure 1.



Figure 1.- Schematic of the sensor

To simulate the crude leak, an infrared laser and a photodetector were installed in the laboratory both using the same wavelength (920nm), this was connected to a 20 meter optic fiber in a closed circuit, whose center was the sensor itself (Fig 2), the system was monitored for 5 minutes without any contact with any hydrocarbon, and this way a baseline of power could be obtained, subsequently the section with the sensor installed was set in contact with crude oil ("Litoral" type) (Fig 3) while still monitoring the system for power changes, the absorbent polymer caused folds in the optic fiber, this generating deacrese of power.



Figure 2.- Laboratory probe schematic

## **Results and Discussions**

Now the graphs obtained as the sensor response are shown (Fig 3), comparing them with another sensor with the same configuration but without using a catalyst.



Figure 3.- Sensors response in the laboratory test

In the obtained results, the augment of sensitivity when using a catalyst in the sensor is noticeable, because both the signal and speed of response are increased, using the catalyst we obtained a maximum drop of 0.3 dB and without it a 0.15 dB was obtained, speaking of speed of response the sensor with a catalyst responds without noise level at 10 seconds, although the sensor without a catalyst responds without noise level at 60 seconds, which is a really significant difference.

## Conclusions

The sensor developed is capable of detecting crude leaks, as a solution for crude leak detection where the crude high viscosity and the big amount of chemicals it contains made it very difficult to sense and detect a leak, so based on time domain reflectometry techniques using an OTDR, developing systems for crude leak detection and localization in tens of kilometers long is achievable.

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# ANALYSIS OF THE EXTRUSION OF LOW-DENSITY POLYETHYLENE BY USING VELOCIMETRY

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The knowledge of the flow kinematics of polymer melts is relevant for their processing as well as for the design of molds and dies. However, the analysis of the flow behavior of polymer melts during extrusion has been typically performed by using rheometrical measurements and numerical simulation. Recently, Rodríguez-González et al. [1, 2] have introduced the use of two dimensional particle image velocimetry (PIV) to study the flow kinematics of polyethylenes in capillaries. In this work, a description of the kinematics of a low-density polyethylene flowing under continuous extrusion through a transparent capillary die was performed by using the PIV technique coupled with rheometrical measurements. The velocity maps for the polymer melt exhibited fully developed flow, meanwhile the flow rate data obtained from the velocity profiles agreed very well with the rheometrical ones. The maximum difference in the volumetric flow rates by using the two methods was 6.5%, which shows the reliability of the PIV technique to describe the flow behavior of the polymer melt. The true flow and viscosity curves for the polymer melt were obtained from the measured wall shear stress and velocity profiles in a wider shear rate range than the accessible by the capillary measurements, including the transition between the Newtonian and power-law regions. This allowed the viscosity data to be very well fitted by a Carreau constitutive equation.

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## FUNCTIONAL POLYETHYLENES INVOLVED IN EFFICIENT COUPLING REACTIONS

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The polyethylene (PE) synthesized in this work is obtained by polymerization of ethylene via coordinative chain transfer polymerization (CCTP) using  $(C_5Me_5)_2NdCl_2Li(OEt_2)_2$  metallocene precursor in combination with MgR<sub>2</sub> followed by efficient functionalization reactions.<sup>1</sup> The Nd complex catalyzed polyethylene chain growth on magnesium to provide dipolyethylenyl magnesium (MgPE<sub>2</sub>). MgPE<sub>2</sub> is further reacted in the same reactor with I<sub>2</sub> to generate an iodo end-functionalized polyethylene (PE-I) in high yield (>95%). PE-I is then modified to introduce reactive groups that can be involved in efficient coupling reactions.

After a nucleophilic substitution with NaN<sub>3</sub>, a polyethylene with an azide end-group (PE-N<sub>3</sub>) is formed and used as a building block<sup>2</sup> in a variety of 1,3-dipolar azyde-alkyne Huisgen cycloaddition reactions.<sup>3</sup> Cyclopentadienyl terminated polyethylene (PE-Cp) was prepared by the reaction between Cp<sub>2</sub>Ni and PE-I. PE-Cp was further used to produce block copolymers via hetero Diels-Alder cycloaddition.<sup>4</sup>



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## EFFECT OF ATMOSPHERIC ETHYLENE-PLASMA TREATMENT ON THE PHYSICOCHEMICAL SURFACE PROPERTIES OF HENEQUEN FIBERS AND ITS INTERFACIAL PROPERTIES WITH HDPE

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A number of surface modification methods have been used on lignocellulosic fibres in the past in order to modify their surface properties, treatments, acetylation, coupling agents, polymer grafting, mercerization, etc.. A more environmentally friendly alternative is the use of plasma technologies. Atmospheric pressure plasma is a ionized gas containing a mixture of ions, electrons, neutral and excited molecules and photons. Depending on the type and nature of the feed gases used, a variety of surface modifications can be achieved, including an increase or decrease of the surface energy, surface cross-linking and the introduction of reactive free groups. The ethylene-plasma treatment duration, magnitude of frecuency and the carrier gas flow over the surface and mechanical properties of henequen fibers, native and mercerized, were studied.

The henequén physicochemical surface properties were characterized by means of XPS, FTIR and SEM. The interfacial shear strength between henequén fibers and High Density Polyethylene was characterized using the pullout micromechanical technique.

The results show that the ethylene-plasma treatments modify both the surface and interfacial properties of the henequen fibers. Moreover, it was found that those changes were more evident for the mercerized henequen fibers than the native ones.

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## EFFECT OF FIBER TREATMENT ON CRYSTALLIZATION OF POLYPROPYLENE IN SUGAR CANE-BAGASSE-PP COMPOSITES. A MODULATED DSC STUDY

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The natural cellulosic fibers as sugar cane bagasse are composed mainly by cellulose, hemicellulose and lignin, which impart them a more hydrophilic character [1]. This property affects the preparation of composites with hydrophobic matrices, so that sometimes final properties decrease as the amount of reinforced material increase. However, natural fibers contain OH groups susceptible to react with substances of non-polar character. This chemical modification gives more hydrophobic character to the physic nature of the surface of fibers, and it can improve the interaction with the matrix at the interface.

In the present work, we present the effect of chemical treatment (silanization, PP grafting and acetylation) onto natural fiber over the crystallization of bagasse fiber-PP composites. The changes of crystallinity of isotactic polypropylene caused by the chemical modification of fibers were followed using a modulated DSC. The interaction of the more hydrophobic surface after treatment with the PP matrix, increase the amount crystallization. So that, the higher extent of chemical modification, the higher is the crystallinity. When an excess of fibers are present, the increase of matrix amount increase the crystallinity until a maximum, after that it decreases by a less nucleation sites.

There were some morphology induction caused by non-treated and treated fibers; this was a consequence of a less or better interaction of the fibers by the matrix. Then, fibers could be functioning as nucleation agents due to the formation of an interfacial transcrystallinity.

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## PRECISION POLYMER SYNTHESIS

## FROM NEW SYNTHETIC PROCEDURES FOR ATRP TO NEW MATERIALS

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Copper-based ATRP (atom transfer radical polymerization) catalytic systems with polydentate nitrogen-based ligands is among most efficient controlled/living radical polymerization systems. [1] Recently, by applying new initiating/catalytic systems, Cu level in ATRP was reduced to a few ppm. Various reducing agents, including metals, organometallic species, sugars, amines, phenols, monomers ligands, radical initiators or electrical current have been successfully applied.[2] Similar control can be achieved with ppm of Fe-based catalysts.[3]

ATRP of acrylates, methacrylates, styrenes, acrylamides, acrylonitrile and many other vinyl monomers provides polymers with molecular weights in a large range 200<Mn<20,000,000 and with low dispersities. Polymers can be formed quantitatively in bulk, in solution and in dispersed media. Water can serve both as solvent for many water soluble polymers and also as medium for microemulsion, miniemulsion, dispersion and suspension polymerization.[4] Block, graft, star, hyperbranched, gradient and periodic copolymers, molecular brushes and various hybrid materials as well as bioconjugates have been prepared.[5] The (co)polymers made by ATRP have many potential applications as components of advanced materials such as coatings, elastomers, adhesives, surfactants, dispersants, lubricants, additives, but also as specialty materials in biomedical and electronic areas and will affect the market of ~\$20 billion/year.[6] Macromolecular engineering comprising design, synthesis, characterization and applications of nanostructured multicomponent polymeric materials prepared via ATRP will be presented.

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## PRECISION ACID, IONOMER, AND IONIC LIQUID POLYMERS

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Precision polyolefins are made using metathesis polycondensation chemistry to regulate, without equivocation, branch identity and the exact location of the branch along a polyolefin backbone [1]. We use precision polyolefin techniques to synthesize a series of acid and ionomers containing polymers, including ionomers that are based on the presence of ionic liquid chemistry. These are extremely tough materials.

The changes in morphology for these precision materials are clearly different from that found in



Fig. 1: X-Ray for Precision Acid Polymer

conventional random ionomers. A high degree of order in the form of layered lamellae becomes apparent in the carboxylic acid polymers that have been formed (Fig. 1)[2]. We also have made a series of phosphonic acid polymers [3], and in addition have research both in sulfonic acid and boronic acid polymers to report. J A C S

X-Ray scattering (Fig. 1) demonstrates a dramatic change in morphology, changing from clusters of ionic groups in conventional ionomers to sheets interconnected via precision hydrogen bonding – the polymer chain remains orthorhombic in spite of such a large

"defect". When the degree of ionic character becomes significant, then a reversion to highly ordered, cubic centered clusters becomes evident (Fig. 2)[4]. Such clusters have never been observed previously.



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## Fig. 2: Cubic Centered Clusters Form When The Concentration of Ionomers Becomes Significant.

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New methods for initiating cationic polymerizations based on the reduction of onium salts by boranes[1,2] and hydrosilanes [3,4] are described. These redox couples can be employed as convenient initiator systems for the homogeneous cationic polymerizations of a wide variety of vinyl and heterocyclic monomers. In this presentation, we report the novel use of a two-component redox system in which a volatile hydrosilane reducing agent is delivered as a vapor to a thin film monomer sample containing the onium salt. Typically, the cationic polymerizations that result are rapid and exothermic. The use of optical pyrometry (infrared thermography) as a convenient method with which to monitor and optimize the aforementioned redox initiated cationic polymerizations is described. Studies of the effects of variations in the structures of the onium salt, the reducing agent and the use of a noble metal catalyst on the polymerizations of typical vinyl and heterocyclic monomers were carried out and will be discussed. Potential applications of this technology include: coatings, adhesives, castings, composites, and electronic encapsulations.

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# LATE AND EARLY TRANSITION METAL CATALYZED CONTROLLED RADICAL POLYMERIZATION OF DIENES

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Living radical polymerization (LRP) enables precise control over molecular weight and polydispersity and has been widely applied in the synthesis of complex macromolecular structures. [1] While catalytic systems based on late transition metals were successful in LRPs mediated by atom transfer radical polymerization (ATRP), dissociation-combination or degenerative transfer and initiated from activated halides or thermal initiators, a broader selection of initiators and catalysts is still needed for the LRP of certain monomers.

1,3-Dienes such as isoprene and butadiene are industrially important, but their controlled polymerization is typically accomplished by anionic or coordination methods requiring stringent conditions. While ATRP works very well with styrene and (meth)acrylates, its extension to dienes has proven troublesome, and with the notable exception of nitroxides and RAFT reagents, metal catalyzed LRP methods have generally failed to control diene polymerizations.

The paramagnetic  $Cp_2TiCl$ , is a mild one electron transfer agent which mediates epoxide radical ring openings (RRO), aldehyde SET reductions and halide abstractions. We have demonstrated[2] the  $Cp_2TiCl$ -catalyzed LRP of styrene initiated by epoxides, aldehydes, halides and peroxides and applied this methodology in the synthesis of branched and graft copolymers.[3] Ti alkoxides generated in-situ from epoxides and aldehydes also catalyze the living ring opening polymerization of cyclic esters, epoxides and anhydrides.

We have previously described the Cp2TiCl-catalyzed isoprene,[5] butadiene and 2,3dimethylbutadiene polymerizations initiated from halides, epoxides, and aldehydes. We will be describing herein a comparison of Ti and Cu diene LRPs and the scope and limitations of each method.

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## PATTERNED POLYMER BRUSHES FOR SURFACE CONTROL

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Precision synthesis of polymer brushes combined with their patterning makes a very powerful tool for surface modification. We report the direct patterning of multi-component block copolymer brush systems [1]. Positive-tone/negative-tone block copolymer brushes have been patterned by electron beam lithographic methods to produce micro- and nanostructures. We have analyzed these systems through variation of polymer brush thickness and investigating different solvent development conditions. Direct patterning of positive-tone/negative-tone block copolymer brushes were also carried out [2]. Their phase separation and morphologies in the patterns was found to be affected by both feature size and development environment.

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# POLYOXETANES: RING OPENING POLYMERIZATION REVISITED FOR NEW POLYURETHANE SOFT BLOCKS AND COATINGS NOVEL PROPERTIES

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Polyurethanes with polyoxetane soft blocks such as P[3FOx] 1 and P[(3FOx)<sub>m</sub>(ME2Ox)<sub>1</sub>.

m] 2 have provided a
rich source of new soft
surface science.
Examples that will be
described include:
(a) Modification of
polyurethanes with soft
blocks containing
quaternary charge (3)

that results in



spontaneous formation of nanopeak and micropeak topologies, (**b**) Better control of ring opening polymerization for more precisely controlled polyoxetane chain architectures (**1**, **2**), (**c**) Development of novel coatings with abhesive surfaces for foul-release applications using soft block **1** together with a new physical model, and (**d**) Development of a new laboratory test that quantitatively measures removal energies associated with weak adhesion (abhesion).

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## ANIONIC SYNTHESIS OF WELL-DEFINED, CHAIN-END AND IN-CHAIN FUNCTIONALIZED POLYMERS

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One of the unique features of living polymerizations, and alkyllithium-initiated polymerizations in particular, is the ability to prepare chain-end functionalized polymers[1]. After complete monomer consumption, the resulting polymeric organolithiums can react with electrophiles to form  $\omega$ -chain-end functionalized polymers[2]. Although many such reactions have been investigated, most of these specific funcitonalization reactions are not quantitative and each must be optimized. It has been of interest to develop general anionic functionalization methods (GFM)[2]. GFM encompass reactions that efficiently introduce a variety of functional groups using the same basic chemistry for all groups. GFM of importance include the reactions of polymeric organolithium compounds with (a) substituted chlorosilanes[3], (b) substituted 1,1-diphenylethylenes[4], (c) substituted alkyl halides[5], and more recently (d) chlorodimethylsilane to form the corrresponding  $\omega$ -silyl hydride-functionalized polymers followed by platinum-catalyzed hydrosilation with substituted alkenes[6]. Herein, the scope and limitations of these general functionalization methods will be described with respect to synthesis of  $\alpha$ -(initiating chain-end), in-chain, and  $\omega$ -(termination chain-end) functionalized polymers.

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# PRECISION POLYOLEFINS VIA 'TWO-STATE' LIVING COORDINATIVE CHAIN TRANSFER POLYMERIZATION

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New paradigms are required that have the potential to dramatically change the range and pace at which specialty polyolefins can be discovered and commercialized. In this regard, we have been pursuing, within a living coordination polymerization system, identification of dynamic fast and reversible bimolecular processes that are competitive with chain-growth propagation and the establishment of mechanistic control points that can provide external control over the relative rates of these processes. In this way, a single catalyst can now be directed to produce, with a high degree of precision, a near continuum of different polyolefin grades that exists between two different limiting stereochemical microstructures, co-polymer compositions or polymer architectures.[1-5] When combined with living coordinative chain-transfer polymerization (LCCTP) that employs an excess of a main group metal alkyl as 'surrogate' chain-growth sites, practical, large-scale production of a broad range of specialty 'precision' polyolefin materials can now be brought closer to realization. This talk will focus on our most recent investigations involving the identification, development, and exploitation of several different classes of two-state LCCTP systems for considerably expanding the range of structure and function for polyolefins.

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## POLYBANK: DEVELOPMENT OF A BANK OF ADVANCED POLYMERIC MATERIALS VIA RAFT TECHNOLOGY AND HIGH THROUGHPUT EXPERIMENTATION

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There is an increasing need by industry and academia to screen a range of polymer materials to evaluate their performance for diverse applications. However, researchers interested in testing such materials in their areas of expertise generally do not have the synthetic skills or infrastructure to prepare them. Consequently, they have to rely on collaborations or commercial suppliers to obtain the materials and often the desired products are not available. This approach can considerably slow the discovery and development process. The development of a bank of advanced polymeric materials (PolyBank) is currently seeking to address this need. PolyBank makes use of highthroughput synthetic techniques currently available at CSIRO and the powerful controlled radical polymerization method developed at CSIRO known as the Reversible Addition Fragmentation chain Transfer (RAFT) Technology. This strategy allows for the systematic, rapid generation and characterization of polymer libraries encompassing a broad range of properties. The RAFT process allows for the preparation of well-defined polymers with predefined molecular weight, chemical composition and architecture. The use of high-throughput synthetic protocols available at CSIRO for RAFT technology can expedite the production of these polymer materials. Many scientific projects would benefit from such a reserve of materials because their researchers could systematically plan their activities based on the polymer resource of PolyBank. This would speed up their investigations and thus accelerate the generation of knowledge and lower the costs of research. This contribution addresses the current status towards the full establishment of PolyBank.

## NITROXIDE-MEDIATED SURFACTANT-FREE EMULSION POLYMERIZATION OF N-BUTYL METHACRYLATE WITH A SMALL AMOUNT OF STYRENE

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SG1 nitroxide-mediated emulsion polymerization of n-butyl methacrylate (BMA) can produce highly living and well controlled polymer chains when polymerized in the presence of 10 mol% styrene (St) using a one-pot, differential monomer addition technique. When n-BMA-co-St is polymerized in the presence of a surfactant above the critical micelle concentration, bimodal particle size distributions are obtained, likely as a result of combined micellar and aggregative nucleation mechanisms. This phenomenon is not observed for the more hydrophilic monomer system of methyl methacrylate and styrene, which yields living, well-controlled polymer with monomodal PSDs. In the absence of surfactant with BMA however, it is possible to prepare stable, monomodal latexes. Using N-tert-butyl-N-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide (SG1), we report the first nitroxide~-mediated polymerization of n-butyl methacrylate with a small amount of styrene in a facile surfactant-free emulsion polymerization system. The surfactant-free system requires no separate macroinitiator synthesis step and produces highly living polymers with monomodal particle size distributions. The initiator efficiency can be greatly improved by the addition of a very small amount of the hydrophilic monomer methyl acrylate in the 1<sup>st</sup> stage. The elimination of surfactant from the system not only allows for better control over the particle size distribution but it is also an important advance for further applications, where the presence of a large quantity of surfactant can be deleterious to both product properties and performance.

## PREPARATION OF FUNCTIONALIZED POLYMERS BY REVERSIBLE ADDITION-FRAGMENTATION CHAIN TRANSFER (RAFT) POLYMERIZATION

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Reversible addition-fragmentation chain transfer (RAFT) polymerization is a polymerization technique that has emerged in the last ten years as may be the most versatile and simple method for the preparation of polymers using a wide range of monomers and controlling their size, architecture and functionality. RAFT polymerization show the main features of a "living" polymerization, therefore the polymers or copolymers prepared in a first step can be re-activated to blockcopolymerize a second monomer. If this second monomer is of a divinyl type, complex polymer architectures can be obtained if the copolymerization conditions are well chosen. In this contribution we report the use of RAFT polymerization to prepare four types of functionalized polymeric materials: 1.- End functionalized ( $\alpha$ ,  $\omega$ ) telechelic polymers with OH, COOH and NH<sub>2</sub> functional groups: 2.-Random functionalized temperature sensitive polymers with acid groups; 3.-Arm functionalized temperature sensitive star-polymers and 4.-Core functionalized nano-gels with temperature sensitive shell. For the first type of functionalized polymer, functionalized dithiobenzoates as chain transfer agents (CTA's) were developed. For the second type of functionalized materials RAFT copolymerization with acid comonomers of methacrylate family were used to taylor the lower critical solution temperature (LCST) of polyNIPAAm. For the third and four type of functionalized materials macro-CTA's were prepared in a first step followed with a second step of RAFT crosslinking polymerization. Adjusting the synthesis variables star polymers and nanogels could be synthesized (Figure 1).



Figure 1: Synthetic scheme for preparation of functionalized star-polymers and nanogels.

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#### SWITCHABLE CHAIN TRANSFER AGENTS FOR RAFT POLYMERIZATION

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In contrast to conventional reversible addition-fragmentation chain transfer (RAFT) agents, acid/base "switchable" dithiocarbamate RAFT agents offer a high level of control over polymerization of both "more-activated monomers" (MAMs, i.e. (meth)acrylates, (meth)acrylamides, styrenics) and "less-activated monomers" (LAMs, i.e. vinyl esters, vinyl amides).[1, 2] This is accomplished by using the "switchable" RAFT agent in either its activated (protonated, controls MAMs) or deactivated (neutral, controls LAMs) form. This new class of RAFT agent allows access to polyMAM-block-polyLAM copolymers, with narrow molecular weight distributions, which are generally unobtainable using conventional RAFT techniques.



Recently, we have demonstrated that the technique is also applicable for the preparation of poly(dimethylacrylamide) in aqueous solution. This study showed that factors influencing acid/base equilibria in the polymerization mixture have a marked effect on polymer dispersity.[3] In this presentation some of the recent developments in the area of "switchable" RAFT will be discussed.

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## NEW ULTRAHIGH MOLECULAR WEIGHT, LOW POLYDISPERSITY AROMATIC POLYMERS FROM METAL-FREE, STEP-GROWTH "CLICK" POLYMERIZATIONS

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According to the classical theory of step-growth polymerization all functional groups at any given stage of the polymerization are equally reactive regardless of the size of the molecule to which they are attached (and that no intramolecular cyclization occurs) [1]. The molecular weight distribution consequently predicted is known as the "most probable" distribution with polydispersity index approaching 2 at high conversion, which means that this type of polymerization is not applicable for the synthesis of polymers with low polydispersity.

Recently, T. Yokozawa has demonstrated [2] that by creating a difference in the reactivity of the functional groups it is possible to transform the polymerization mechanism from a step-growth to a chain-growth. A number of polymers with low polydispersity and moderate molecular weight have been obtained successfully.

Several years ago, for the first time we reported on application of superelectrophilic chemistry for the preparation of novel, high molecular weight linear polymers by superacid catalyzed polycondensation of carbonyl-containing compounds with non-activated aromatic hydrocarbons [3]. The reactions were shown to be tolerant of such functional groups as hydroxy, sulfoxy, amino, carboxy, and cyano [4-5].

The report presents a general overview of novel polymer syntheses involving superelectrophiles. Preparations of Ultra High Molecular Weight ( $Mw > 1\ 000\ 000$ ) and low polydispersity (Mw/Mn = 1.15 - 1.25) aromatic polymers by metal-free, room temperature, superacid catalyzed "click" - polyhydroxyalkylation are discussed. Unusual mechanism of step-growth polyhydroxyalkylations leading to the polymers with low polydispersity is presented.

Cheaply available monomers, metal-free, stoichiometric and non-stoichiometric syntheses and the promising properties of the new polymers that might be obtained will make superelectrophilic reactions a powerful tool in polymer chemistry.

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## BIOMIMETIC SYNTHESIS OF PEDOT CATALYZED BY MCM/41 SUPPORTED HEMATIN

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Polyethylenedioxytiophene (PEDOT) has been one of the most studied conjugated polymers in the last years due to its interesting electro-optic properties. This polymer can be synthesized from 3,4 ethylenedioxythiophene (EDOT) monomer. PEDOT has good film properties, shows electrical conductivity and exhibits properties to use it in electrochromic devices, among other applications [1]. The most used synthetic procedures up today for PEDOT synthesis imply highly oxidant and low pH conditions which are not compatible with biological systems [2,3]. In this work the use of a biomimetic catalyst based on hematin supported in MCM-41 was studied for EDOT polymerization in acidic conditions; oxidation around pH 2 in the presence of polystyrenesulphonate (PSS) as doping and stabilizing agent and hidrogen peroxide as oxidant agent was carried out. Biomimetic reaction yields were evaluated under different reaction conditions as well as the recycling capacity of the biomimetic catalyst. The results showed that it can be used an small amount as 5 mg of hematin/MCM-41 catalyst to obtain PEDOT/PSS and that it can be reused up to 9 times without significant yielding loss, which was maintained between 80%-65%. Furthermore, it was also established thorough UV/Visible and FTIR spectroscopy that chemical properties of obtained PEDOT are comparable to those obtained by other synthetic methods and that this also remain even when the oxidant concentration was changed. This last indicated that the biomimetic catalyst Hematin/MCM-41 is stable under the studied reaction conditions; hence it represents a viable, low cost alternative, for PEDOT obtaining.

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## NOVEL SPIROORTHOCARBONATE DERIVED FROM FLUORENE AS ANTISHRINKING AGENT FOR THE CATIONIC PHOTOPOLYMERIZATION OF BISGLYDICIL ETHER BISPHENOL A (BADGE)

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## Abstract

In this work was prepared the spiroorthocarbonate FSOC derived from fluorene. After characterization by FTIR and NMR spectroscopy, the synthesized FSOC was evaluated as antishrinkage additive in the cationic photopolymerization of bisglycidil ether of Bisphenol A (BADGE). The FSOC was mixed with BADGE at 2.5, 5 and 10 % mol. It was found that the shrinkage decreased with increased concentration of FSOC. At the higher concentration of FSOC not only was eliminated the shrinkage but it was achieved small level of expansion. The presence of FSOC did not interfere with the photopolymerization rate of BADGE.

## Introduction

Shrinkage is a phenomenon inherent in all the processes of polymerization. It is defined as the reduction in volume caused by an increase in density. This is due to the formation of covalent bonds during the polymerization process. The shrinkage can be an adverse factor in certain applications, such as the development of composite materials, materials for electrical insulation, manufacture of optical fiber and the preparation of dental materials polymeric.

To avoid shrinkage in the polymers are used a type of compounds as spiroorthocarbonates (SOCs) that are monomers that show volume expansion during the polymerization. The efficiency of SOCs relies in the fact that they undergo double ring opening polymerization and in this process for every bond that goes from a Van der waals distance to a covalent distance [1]. This is the reason why the polycyclic monomer ring-opening polymerization occurs essentially with zero shirinkage or expansion upon polymerization [2].

Taking into consideration the efficiency demonstrated by the spiroorthocarbonates to reduce or eliminate shrinkage [3-5], in this research is reported, the preparation of a new spiroorthocarbonate from an aromatic compound as the flourene (FSOC). This FSOC was elaborated through of the reaction of transeterification of tetraetilorthocarbonate with Fluorenediol. Once that the FSOC was syntetized it was evaluated as antishrinkage additive in the cationic photopolymerization of bisglycidil ether of Bisphenol A (BADGE)

## Experimental

Synthesis of Spiroorthocarbonate from Flourene (FSOC)

In a three-necked, 50-mL, round-bottom, flask provided with magnetic stirrer, condenser, nitrogen inlet and thermometer were placed 2 g of molecular sieves and 40 mL of diethyl ether. Then 4 g

(0.01769 mol) of FDiOH and 0.0487 g (2.8 x 10-4 mol) of p-toluensulfonic acid. After of 5 min was added 1.47g (0.00766 mol) of tetraethyl orthocarbonate and 8.93 x10 -2 g (0.008428 mol) of Na2CO3. The system was flushed with nitrogen to set anhydrous conditions for 9 h at room temperature. The reaction mixture was filtered and the molecular sieves were separed washing with chloroform that was rotaevaporated. The compound FSOC was characterized by FTIR and RMN

Cationic Photopolymerization of the FSOC

UV curing procedure and shirinkage measurements of FSOC

Phtocurable formulations were prepared by the addition of the FSOC monomer to the epoxy monomer Bisphenol A (BADGE), that was used as epoxy matrix, in the range between 2.5 and 10 wt %. In all the mixtures 1 wt% of cationic photoiniciator (4-n-decyloxyphenyl) phenyliodonium (DPPI) was added. The formulations were coated and irradiated with a UV lamp, for 30 min in air a light intensity on the surface of the samples of about 10.7 mW/cm2. RT-FTIR was used to monitor the kinetics of photopolymerization of the FSOC.

Shirikage measurements were obtained by measuring the density of the systems before and after curing. The solution density (before curing) was measured by weighing a precise amount of liquid formulation. The density of cured films (after curing) was measured by means of a Startorius balance YDK01 with density determination kit. The Archimede principle is applied for determining the specific gravity of a solid with this measuring device: a solid immersed in a liquid is exposed to the force of buoyancy. The value of this force is the same as that of the weight of the liquid displaced by the volume of the solid. The density measurements have been performed with the Sartorius hydrostatic balance which enables to weigh the solid in air as well as in a liquid, the specific gravity of the solid is determined when the density of the liquid causing buoyancy is known, through the following formula:

$$\rho = \frac{W(a) \cdot \rho(l)}{W(a) - W(l)}$$

Where:  $\rho$  = specific gravity of the solid:  $\rho(l)$  = density of the liquid; W(a) = weigth of the solid in air; W(l) = weigth of the solid in liquid.

The chosen liquid was ethanol with a density values of  $25^{\circ}$ C of d25 = 0.78506 g/ml. The specific volume of the system before and after curing was defined as the inverse of the density and the shirinkage was calculated with the following formula:

$$\Delta = \frac{Vs - VL}{VL} \times 100$$

Where:  $\Delta$  = volume change ; Vs = specific volume of the cured polymer; VL = specific volume of the liquid formulation;

#### **Results and Discussion**

Synthesis of the monomer spiroorthocarbonate of flourene (FSOC).

The synthesis of the FSOC was successfully achieved using two stages process. First, for the synthesis of the FDiOH the product resulted by the nucleophylic addition of the anion derived of the flourene that is added as p-formaldehyde producing the diol (FDiOH) as a white powder that was obtained in a 80% yield with melting point of 142-145°C. (Figure 1). The FDiOH was identified by 1H NMR (300MHz), where different signals were identified in the range 7 -8 ppm corresponding to the aromatics and the appearance of a doblet at 4.05 ppm which corresponded to the methylene and at 2.07 ppm a triplet that corresponded to the hydroxyl group.



Figure 1. Schematic illustration of synthesis of FDiOH

In the second stage the FDiOH was reacted by means of the transesterification with tetraethyl orthocarbonate (TEOC) in the presence of p-toluensulfonic acid as is shown in the Figure 2, where a white powder was obtained with a m.p. of 238- 240°C at 93.75% yield. The proton spectrum of obtained for the FSOC showed the peaks at 7-8 ppm corresponded to the protons of the aromatic moiety, whereas the peaks at 4.3 ppm corresponded to the protons of the carbons of the oxygens of the spiroothocarbonate moiety.



Figure 2. Schematic illustration of synthesis of FSOC

The Figure 3 displays the IR spectra of the flourene and the two synthetized compounds: FDiOH and FSOC. It can seen that the flourene has a peak characteristic for aromatic compounds at 758 cm-1 and a peak at 2916 cm-1 which corresponded at aliphatic C-H. when the FDiOH is formed

the IR spectra shows two signals: a broad peak at 3318 cm-1 and 1028 cm-1 which corresponded at C-O group. The IR spectra of the FSOC completely disappeared the peak at 3318 cm-1 and appearance the peaks characteristic for spiro orthocarbonate groups located at 1196, 1113 y 1041 cm-1.



Figure 3. spectra IR of the Fluorene, FDiOH and FSOC

Photopolimerization of FSOC with UV ligth and photoiniciator DPPI.

Once that the FSOC monomer was obtained, it was photopolimerized with BADGE, used as epoxy matrix. In the Figure 4 can be seen the polymer from the FSOC monomer when it is photopolimerized (P-FSOC) with photoiniciator DPPI.



Figure 4. Polymer from FSOC when is photopolimerized (P-FSOC)

Determination of Kinetics of ring opening by cationic photopolimerization of the formulations of BADGE at different concentrations of FSOC monomer.

The FSOC was added to the BADGE epoxy resin in concentrations of 2.5, 5 and 10 wt %. In

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Figure 5 the conversion curves as a function of irradiation time are reported for FSOC monomer. The curves give an indication of the rate of polymerization. It is evident the high reactivity to an intensity of UV light as low as 10 mW/cm2. The reactions of photopolymerization proceeded rapidly in all cases, reaching conversions between 50 and 60 % in the first 50 seconds and conversions levels between 70 and 80 %. Given that concentrations of FSOC were not very high, the speed of photopolymerization of BADGE is not significantly influenced by the presence of the FSOC which is good thing, because it is known that spiroorthcarbonates generally have speeds of cationic photopolymerization lower than the epoxy monomers, resulting in a reduction in the speed of photopolymerization of these when are add the SOCs as antishirinkage additives.



Figure 5. Real-time conversión curves as a function of irradiation time for the pristine BADGE epoxy monomer (0% FSOC) and for the formulations containing increasing amount of FSOC monomer. Was used for all the formulations 1wt% of DPPI photoiniciator and a UV light intensity of 10.7 mW/cm2.

#### Shirinkage measurements

The efficiency of the FSOC as low shrinkage additive was evaluated by adding of different concentrations of this compound in the monomer BADGE and measuring the specific density of the starting formulations and the corresponding cured films. The density values together with the calculated shrinkage are reported in the Table 1.

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Formulations	Volumen changes (%)	
BADGE	-4.77	
BADGE + 2.5 % FSOC	-2.42	
BADGE + 5 % FSOC	-1.94	
BADGE + 7.5 % FSOC	-1.56	
BADGE + 10 % FSOC	0.19	

Table 1. Volume changes during UV curing with different formulations of BADGE-FSOC.

An important decrease on shirinkage extent upon photopolymerization was evidenced in the cured films obtained in the presence of FSOC monomer. It can be observed that pristine BADGE

showed a realtive value of -4.77 for the shirinkage while that increasing concentration of FSOC resulted in a decrease of the shrinkage and at 10 wt% it was observed a positive value of 0.19.

## Conclusions

FSOC was syntetized and obtained in a 93wt% yield, with the aim to reduce shrinkage during cationc photopolymerization of the epoxy monomer BADGE. The analysis of volume change revealed that FSOC not only was eliminated the shrinkage but it was achieved small level of expansion 0.19 % when 10 wt % was used.

## Acknowledgements

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# HETEROGENEOUS ETHYLENE AND ALFA-OLEFINS COPOLYMERIZATION USING ZIRCONOCENE ALUMINOHYDRIDE COMPLEXES

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## Abstract

Linear low density polyethylene (LLDPE) is one of the most important commercial polyolefin due to its useful applications in several areas and particularly in the film industry.[1] LLDPE is commercially produced using Ziegler-Natta or metallocene catalysts. Even though Ziegler-Natta products still dominate the market, metallocene-made LLDPE resins have several attractive properties, such as high incorporation levels of alfa-olefins with uniform chemical composition distribution.[2]

In this work we studied the copolymerization of ethylene and different alpha-olefins (propylene, 1butene, 1-hexene, and 1-octene) using aluminohydride zirconocene systems supported on modified silica. The copolymerization reactions where carried out in hexanes, at different Al/Zr ratios, using two different comonomers concentrations. The effect of comonomer type on catalyst activity and polymer molecular weight and chemical composition distributions (MWD and CCD) was compared. Average comonomer incorporation was determined by 13C NMR and the CCD by crystallization elution fractionation (CEF).

Most of the copolymerizations showed very high catalytic activity (up to 4000 Kg PE/mol Zr), and the molecular weight was higher for the copolymers containing 1-octene, demonstrating that aluminohydride zirconocene systems can copolymerize ethylene and alpha-olefins effectively.

## Introduction

Linear low density polyethylene is one of the most important polyolefin, due to its useful applications in several areas, particularly in the film industry for packing, insulation, film coating and co-extrusion. In polymer blends with others high density or low density polyethylene, LLDPE has been used for pipe applications in agricultural or as filler in resin formulations to provide flexibility to the materials.1 As is known, LLDPE is produced by coordination polymerization using Ziegler-Natta or single site catalysts, mainly in slurry or gas phase processes. Even though most of the commercial LLDPE is currently produced with conventional Ziegler-Natta catalysts, an important increase in the production of LLDPE with single site catalysts has been observed in the last years,2 due to the improved properties obtained for this polyethylene, using metallocenes or constrained geometry catalysts (CGC).3 Metallocene-made LLDPE resins (mLLDPE) have several attractive properties, such as high incorporation levels of alfa-olefins with uniform chemical composition distribution. Homogeneous comonomer incorporation improves properties as greater stiffness and impact strength, greater stretch and puncture resistance, and better sealability as compared to LLDPE produced by conventional Ziegler-Natta catalysts.

Comonomer incorporation depends mainly on the metallocene structure, where the ligand configurations control stereo regularity, molecular weight distribution, and uniform comonomer

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composition in the polymers.4 Many kind of metallocene complexes have been studied and reported in the homo and copolymerization of different olefins and alfa-olefins. Most of the literature reports the use of monometallic complexes, and just a few mentions the use of dinuclear or heterobimetallic complexes for olefins and alfa-olefin copolymerizations.5 Some years ago, we reported the use of zirconocene aluminohydride complexes for ethylene polymerizations, comparing their performance with the corresponding zirconocene dichloride, under the same polymerization conditions. Zirconocene aluminohydride showed higher activities 30-40% than zirconocene dichloride, when were activated with MAO in solution, under the same polymerization conditions.6

In this work we studied the copolymerization of ethylene and different alfa-olefins (propylene, 1butene, 1-hexene, and 1-octene) using zirconocene aluminohydride systems, supported on modified silica. The copolymerization reactions were carried out in hexanes at different Al/Zr ratios of supporting, using two comonomer concentrations. The effect of the comonomer type on the catalyst activity and polymer molecular weight and chemical composition distributions (MWD and CCD) was compared. Average comonomer incorporation was determined by 13C NMR and the CCD by crystallization elution fractionation (CEF).

## **Experimental**

#### Materials

nBu-Cp2ZrCl2 (98%, Strem), LiAlH4 (1M solution in diethyl ether, Aldrich), methylaluminoxane (PMAO, 10 wt.-% solution in toluene, Aldrich), ethylene (99.9%, Praxair), were used as received. Comonomers, Propylene (99.9%, Praxair) and 1-butene (99.99%, Sigma-Aldrich) were used as received. 1-Hexene (99%, Aldrich) and 1-octene (98%, Aldrich), were distilled under atmospherical pressure before using.

Solvents, diethyl ether, toluene, and hexane, (Aldrich) were purified by passing through columns packed with activated alumina and molecular sieves (Zeolum Type F-9, Tosoh Co.) and stored with 3A/4A mixed molecular sieves.

## Polymer Characterization

Molecular weight and polydispersity were measured by gel permeation chromatography (GPC) in a Gel Alliance GPV 2000 instrument at 140oC. The equipment used three styragel columns, and was coupled to a refractive index (IR) detector (480 nm) and to a multi-angle light scattering (LS) detector (690 nm). 1,2,4-Trichlorobenzene was used as solvent, at a flow rate of 1mL/min. The columns were calibrated with narrow molar distribution polyethylene standards.

Differential scanning calorimetry analyses were performed on a modulated TA Instrument 2920, at a heating rate of 10oC/min on a temperature range from 50 to 160oC. Through a second heating cycle the thermal and mechanical history of the samples was eliminated.

Comonomer incorporation was determined by 13C NMR spectroscopy in a JEOL Eclipse 300. The 13C NMR spectra were obtained in the equipment operating at 75 MHz. Sample solutions of polymers and copolymers were prepared in tetrachloroethylene using deutered benzene as external reference.

## Synthesis of nBu-Cp2ZrH3AlH2

All the operations were carried out on a standard high-vacuum line or in a dry-box under nitrogen (99.999% from Praxair).

The nBu-Cp2ZrH3AlH2 was synthesized as reported in a previous work, based on the zirconocene aluminohydrides syntheses reported by Stephan and co-workers.[7] A solution of nBu-Cp2ZrCl2  $(3.2\times10-3 \text{ mol})$  in diethyl ether (20 mL) was stirred at 0oC and 2.2 equiv of LiAlH4 (7.07×10-3 mol) in diethyl ether was dropped during 10 min. The formation of a fine white powder was observed when the mixture was allowed to warm to room temperature (30 min) and the solution was filtered. The diethyl ether was evaporated to provide the corresponding zirconocene aluminohydride in quantitative yield, which was dissolved in tolulene (30 mL).

Supporting of the pre-catalyst (nBu-Cp2ZrH3AlH2/SiO2/MAO)

The supported pre-catalyst was prepared according to the method reported for metallocene complexes.7

15 mL of a10 wt.-% solution of PMAO (without TMA) in toluene was added to a suspension of SiO2 (1 g Sylopol 948/20 mL of toluene), previously dehydrated for 6 h at 800oC. The addition of the PMAO solution was carried out at 0oC, and then the mixture was allowed to warm to room temperature for 1 h. Then, suspension was heated at 50oC for 2 h. The slurry was filtered and washed twice with toluene to obtain the modified silica (SiO2/MAO).

A toluene solution of nBu-Cp2ZrH3AlH2 ( $3.2 \times 10-3 \text{ mol/30 mL}$  toluene) was dropped to 1 g of modified silica (SiO2/MAO) suspended in 30 mL of toluene, using Al:Zr molar ratio (50:1), according to formulations reported in the literature for highly active supported metallocenes. [10] The addition was carried out at 0oC an then the mixture was stirred for 12 h at room temperature. The slurry was filtered, washed twice with toluene and dried in vacuum for 6 h. The content of Zr (1.97 wt.-%) was determined by atomic absorption (AA), and the supported pre-catalyst nBu-Cp2ZrH3AlH2/SiO2/MAO was stored in a glove box.

Polymerization and Copolymerization Reactions

Polymerization and copolymerization reactions were carried out in a 600 mL Parr reactor equipped with temperature controller, Ar, ethylene and solvent inlets. Before each polymerization, the reactor was heated under vacuum for 1 h at 150oC and purged with N2 several times.

The reactor was charged successively with hexane, the cocatalyst solution (PMAO-7, 10 wt.-% in toluene), and the corresponding amount of comonomer (propylene, 1-butene, 1-hexene or 1-octene). The mixture was allowed to react as "scavenger" for 30 min, and the pre-catalyst (nBu-Cp2ZrH3AlH2/SiO2/MAO) suspended in hexane was finally added to the reactor. The polymerization started by addition of ethylene. Polymerization and copolymerization conditions for all the runs were as follows: ethylene 65 psig, 150 mL of hexane, polymerization temperature of 70oC, comonomer addition propylene, 1-butene, 1-hexene or 1-octene (0.1 and 0.2 M), and polymerization time of 0.5 h.

The polymerization was stopped by rapid depressurization of the reactor, the polymer was washed one time with acidified methanol (10 wt.% HCl), then rinsed with methanol, and dried in a vacuum oven for 4 h at 60 oC.

## **Results and Discussions**

Preliminary ethylene homopolymerizations were carried out with the zirconocene aluminohydride complex supported on Sylopol-948 silica modified with MAO. Zr and Al (7 wt.% and 2.3 wt.% respectively, on the supported silica) were measured by inductively coupled plasma-optical emission spectroscopy (ICP, Teledyne Leeman Labs, Prodigy High Dispersion ICO). Results and reaction conditions for these reactions are summarized in Table 1.

The nBu-Cp2ZrH3AlH2/SiO2/MAO supported on Sylopol-948 silica showed high activities and

productivities, as expected, even at low Al/Zr ratios (additional MAO as co-catalyst). According to the above results, an Al/Zr ratio around 2000 was set for the copolymerization reactions performed in this work.

Copolymerization reactions of ethylene with propylene, 1-butene, 1-hexene and 1-octene were studied under similar conditions, using the zirconocene aluminohydride system.

With the exception of propylene, other comonomers were added at two different concentrations, and loaded at the beginning of the copolymerization reactions.

Table 1. Preliminary ethylene polymerizations using nBu-Cp2ZrH3AlH2/SiO2/MAO supported on Sylopol-948 silica.

Exp.	[Cat] 10-6	Co-Cat	PE	А	Р
	mol	(Al/Zr)	(gr)	KgPE/molZr h	KgPE/gr Cat
1	2.0	3,250	7.1	46,100	1,900
2	4.1	2,000	6.1	19,500	800
3	1.7	2,000	3.2	25,100	1,000
4	6.6	1,700	3.4	6,942	283
5	4.2	800	5.9	18,600	770

T = 70oC, 150 mL hexane, PC2= 65 psig, 500 rpm, t = 0.5 h

Figure 1 shows the ethylene flow consumption in the copolymerization reactions with  $\Box$ -olefins compared with the flow consumed in the ethylene hopolymerization under similar conditions. As can be observed in this figure, homopolymerization reaction was more slowly activated than copolymerizations, probably due to the "comonomer effect", which could produce higher activation rates in the reactions; however, the final activities for propylene, 1-butene and 1-hexene



Figure 1. Ethylene flow consumption versus polymerization time in ethylene homo and copolymerization reactions --- C2, --- C2-C3, --- C2-C4 --- C2-C6, --- C2-C8.

Ethylene and 1-octene copolymerizations showed the highest activities, as reported for other metallocene systems.8 Table 2 summarizes copolymerization conditions and results obtained for these reactions. Most of the Defins, were probed at two concentrations, what could affect the

activity of the systems and the molecular weight of the copolymers.

As has been reported for other metallocene systems, a negative "comonomer effect" related to the activities of the systems, is observed when using propylene, 1-butene and 1-hexene as comonomers, where the lowest values were presented in 1-butene reactions.9

A decrease of 30% in activity was observed in copolymerizations of propylene, compared to the activity showed in experiment 2 (ethylene homopolymerization), 79 and 65% lower in 1-butene and 1-hexene copolymerizations, respectively, and just in the case of 1-octene the copolymerizations showed a positive effect between 30 - 40% in activity increase.

As for 1-octene reactions, the decrease in the addition of comonomer (Exp. 13-15) led to the increase of the copolymerizations' activity, however, incorporation grade of this copolymer resulted the lowest for this set of experiments.

The molecular weights obtained for the copolymers synthesized with any type of alfa-olefin, were drastically decreased, probably due to the increase of the termination reactions, when comonomer concentration increases.

Exp.	Сор	[Comonomer]	A	Mw	Mw/Mn
	(mol/L)	mol/L	KgPE/molZr h	(g/mol)	
2	HDPE*	-	19,500	269,552	2.7
7	Propylene	0.17	12,500	21,603	2.7
8	Propylene	0.2	13,600	19,333	2.9
9	1-butene	0.28	4,200	11,033	2.8
10	1-butene	0.17	4,000	110,879	3.6
11	1-hexene	0.28	6,700	20,590	2.6
12	1-hexene	0.17	5,600	50,868	2.8
13	1-octene	0.28	24,800	43955	2.7
14	1-octene	0.28	22,500	36,337	2.9
15	1-octene	0.17	32,900	63,422	2.8

Table2.CopolymerizationsofEthyleneandDifferentComonomersusingnBuCp2ZrH3AlH2/SiO2/MAOSupported on Sylopol-948silica

T = 70  $\overline{\text{OC}}$ , 4.0- 5.7 X 10-6 M Cat, 150 mL hexane, PC2= 65 psig, Al/Zr = 2000 -2400, 500 rpm, t = 0.5 h \* C2 homopolymerization.

Average comonomer incorporation was determined by 13C NMR using a Bruker DRX spectrometer operating at 166.66 MHz.

Table 3 shows the incorporation percent, obtained at high comonomer additions (0.2 M), where propylene showed the highest incorporation (21%, Exp. 8), followed by 1-butene and 1-hexene

(8.2 and 8.0 mol %, Exp. 9 and 11, respectively).

Comonomer incorporation grade has been related to the steric hindrance produced by the  $\Box$  olefins in the copolymerization reactions. As expected, the lowest incorporation was observed for 1-octene (Exp. 13, Table 3), which can produce long chain branchings in the copolymers.

Exp.	Сор	Comonomer	Comonomer
	(mol/L)		mol %
			Incorporated
8	0.2	Propylene	21.5
9	0.28	1-butene	8.2
11	0.28	1-hexene	8.0
13	0.28	1-octene	5.8

Table 3. Comonomer addition and incorporation in copolymerization reactions

The chemical composition distribution (CCD) of the comopolymers was obtained by crystallization elution fractionation technique (CEF), using a Polymer ChAR instrument, and 1,2,4-trichlorobenzene as elution solvent.



Time (min)



The CEF analyses of the copolymers were determined with a total analysis time of 140 minutes. A fast crystallization and heating rates of 3oC /min was performed for each experiment, where the separation of two fractions were detected for all the copolymer samples as shown in figure 2.

CEF analysis of HDPE obtained at similar polymerization conditions to that of copolymerization reactions is also showed in figure 2 (curve in black) in order to compare the number and type of components fractionated according to their crystallization behavior.

As is observed in figure 2, the chemical composition curve for HDPE (curve in black) shows a bimodal distribution, which could be expected for the heterobimetallic catalytic system used in these experiments. Two components shifted to lower crystallization temperatures were separated for the copolymers obtained with propylene, 1-butene, 1-hexene and 1-octene, where the highest

comonomer concentration, was found in ethylene-propylene copolymer, as calculated by NMR in 21 mol %.

## Conclusions

The activity of the supported zirconocene aluminohydride system (nBu-Cp2ZrH3AlH2/SiO2/MAO) was probed in the copolymerization of ethylene with different comonomers (propylene, 1-butene, 1-hexene and 1-octene). Copolymerizations performed with 1-octene showed the highest activity but the lower comonomer incorporation (5.8 mol %). Copolymerizations carried out with propylene, showed the highest degree of comonomer incorporation, maintaining high levels of catalytic activity.

According to the above results, we conclude that nBu-Cp2ZrH3AlH2/SiO2/MAO system can be useful in obtaining homogeneous linear low density polyethylene (mLLDPE).

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# HOMOGENEOUS RADICAL POLYMERIZATION OF 2-HYDROXYETHYL METHACRYLATE CATALYZED BY CATIONIC RUTHENIUM(II) COMPLEXES. INFLUENCE OF COUNTERION.

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#### Abstract

Cationic coordinatively saturated complexes of ruthenium(II), [Ru(o-C6H4-2-py)(phen)(MeCN)2]+, bearing different counterions of PF6- and Cl- have been used in the radical polymerization of 2-hydroxyethyl methacrylate in protic media, and acetone, under homogeneous conditions. Exchange of PF6- by Cl- increases the solubility of the complex in water. Both complexes led to the fast polymerization under mild conditions but control was achieved only in organic solvents and was better for the complex with Cl-. The polymerization accelerated in aqueous media and proceeded to a high conversion even with a monomer/catalyst = 2000/1, but without control. Polymerization mediated by complex bearing Cl- was slower in protic solvents but faster in acetone and always resulted in lower molecular weight polymers. Thus, the nature of the anion strongly affected the catalytic activity of the complexes and may serve as way of fine-tuning the catalytic properties.

#### Introduction

2-Hydroxyethyl methacrylate (HEMA) is a commercially important monomer, and can be polymerized directly, as is, only via radical mechanism producing hydrophilic polymers [1]. Since in free radical process control over the molecular weights and terminal groups of the polymer is nearly impossible, controlled/living radical polymerization approach should be an optimal choice for the polymerization of HEMA. Metal-catalyzed or atom transfer radical polymerization (ATRP) is one of the most versatile methods for controlled polymerization of different monomers and synthesis of well-controlled homo- and co-polymers of non-protected HEMA by ATRP in different solvents has been reported using both copper and ruthenium-based catalysts [2-4]. However, despite the recent success of the ATRP approach for synthesis of hydrophilic polymers, the number of catalytic systems which permit the controlled polymerization in protic, particularly aqueous media, is still very limited. The copper-based catalysts suffered undesirable side reactions, that requires high content of the catalyst [3]. The ruthenium-catalysts generally are more tolerant to both hydroxyl-functional group and the presence of water, but the grand majority of the ruthenium catalysts so far used in ATRP have limited solubility in protic solvents, and especially in water [4].

This study deals with the direct homopolymerization of HEMA mediated by two cationic cyclometalated ruthenium complexes differed only by anions,  $[Ru(o-C_6H_4-2-py)(phen)(MeCN)_2]PF_6$  and  $[Ru(o-C_6H_4-2-py)(phen)(MeCN)_2]Cl$  (**Ia** and **Ib** in Fig. 1) under mild conditions. Catalysts of this kind have been reported for controlled/living radical polymerizations of traditional hydrophobic monomers [5]. Because of their ionic nature these complexes are reasonably soluble in protic solvents and this represents a considerable advantage for the polymerization of hydrophilic monomers. Kinetic features of the polymerization and the catalytic behavior of the complexes in different solvents: acetone, methanol, methanol-water

mixtures and pure water have been investigated. It has been shown that counterion has very strong effect on activity of the catalyst and controllability of the polymerizations in both protic and aprotic media.

# Experimental

## Synthesis of the catalysts

The complex 1a, bearing PF<sub>6</sub>-, was synthesized according to the reported procedure [6] and complex 1b, with Cl- anion, was prepared by the ion exchange reaction using activated *amberlite* column. The complexes were characterized by <sup>1</sup>H NMR, <sup>31</sup>P NMR, IR and MS techniques.



Figure 1. Structures of the catalysts.

## **Polymerization procedures**

*Homopolymerizations* were conducted in solutions (50/50 v/v) using the Schlenk technique. Homogeneous solutions were formed immediately at room temperature and the reaction tubes were immersed in an oil bath preheated at the desired temperature. The polymerizations in acetone and MeOH were carried out at 50 °C and in water at 40 °C. In the majority of the experiments, the initial molar ratio of [Monomer]<sub>0</sub>/[Catalyst]<sub>0</sub>/[Initiator]<sub>0</sub> = 200/1/1 was held. Ethyl-2bromoisobutyrate (EBiB) was used as an initiator. The conversions were determined gravimetrically and the current monomer concentration, [M], was determined by subtraction of the amount of the polymer from the initial monomer. The molecular weights and molecular weight distribution were analyzed by GPC (Waters 717) equipped with RI detector using 10 mM solution of LiBr in DMF as an eluent. The polymer samples were injected in GPC without purification. Radical mechanism of the polymerizations was confirmed using TEMPO as radical scavenger in MeOH and water reactions.

*Chain Extension Experiments* were conducted under identical conditions to the homopolymerizations, using as a macroinitiator PHEMA previously synthesized with **Ib** and EBiB in MeOH at  $50^{\circ}$  C within 20-25 % of conversion. The PHEMA macroinitiator was purified passing through a silica column, dried in vacuum and then applied as a initiator for the next polymerization of HEMA.

## **Results and Discussion**

Semilogarithmic kinetic plots and evolution of the molecular weights  $(Mn,_{GPC})$  with conversion for the polymerizations catalyzed by **Ia** in MeOH and acetone at 50° C are depicted in Fig. 2. Both polymerizations were fast and proceeded to high conversions. An insignificant acceleration observed in acetone after 4 h of the polymerization (60% conversion) may be explained by "geleffect" since acetone is a poor solvent for PHEMA, but the effect was very weak compared to that reported for the free radical polymerizations [7]. The Mn obtained by GPC were higher than the calculated values (shown by dashed line in Fig.2) but increased almost linearly with conversion in

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both solvents and the polymers of very similar molecular weight were obtained at the end of the reactions (Mn GPC = 36800 at 82% in MeOH and 43800 at 87% in acetone), but MeOH polymerization resulted in less polydisperse PHEMA.



**Figure 2.** Kinetic plots and evolution of the molecular weights (Mn,GPC & PDI) with conversion for polymerizations of HEMA catalyzed by **Ia** at 50 °C in methanol ( $\bullet$ ) and acetone ( $\blacksquare$ ).

Complex **Ia** is soluble in organic protic solvents, but is insoluble in water even at elevated temperatures. In order to investigate how the hydrophilic nature of the catalyst may affect the polymerization, several polymerizations mediated by **Ib** were carried out. This complex is structurally identical to **Ia** and the only difference between them is the counterion (see Fig. 1). Exchange of  $PF_{6}$ - by Cl- allowed to improve dramatically the solubility in water and at the same time did not affect other important properties (reduction potential, extinction coefficients, etc.). The important role of counterion for both copper and ruthenium catalysts in ATRP has been discussed in several publications, and it has been shown that counterion has a strong influence on the catalytic activity and on the control in the polymerization [8]. However, the information available on the nature of this phenomenon remains limited, particularly for ruthenium, since the grand majority of the complexes studied so far are neutral.

Data of the HEMA polymerization mediated by **Ib** in MeOH, acetone and water are presented in Fig. 3.



**Figure 3.** Kinetic plots and evolution of the molecular weights (Mn,GPC & PDI) with conversion for polymerizations of HEMA catalyzed by **Ib** at 50 °C in methanol (•) and acetone (•) with the initial molar ratio of  $[HEMA]_0/[Ib]_0/[EBiB]_0 = 200/1/1$  and water at 40 °C with the initial molar ratio of  $[HEMA]_0/[Ib]_0/[EBiB]_0 = 200/0.1/1$  ( $\blacktriangle$ ).

Surprisingly, the polymerization catalyzed by **Ib** was faster in acetone but slower in MeOH than that mediated by **Ia** under similar conditions (compare Fig.2 and 3) but resulted in lower

molecular weight polymer in both cases. GC analysis demonstrated that more than 90% of EBiB was consumed in first 30 min in the reaction mediated by **Ib** and only 60% in that mediated by **Ia**. Thus the higher molecular weight PHEMA synthesized with **Ia** may be explained by relatively low efficiency of the initiator in these polymerizations. The dependence of Mn on conversion was linear for the MeOH and acetone polymerizations catalyzed by **Ib**; PDIs abruptly narrowed in acetone and were quite narrow at high conversions (below 1.3). Taking into account the difference between the real molecular weight determined by <sup>1</sup>H NMR and the molecular weight obtained by GPC calibrated by PMMA standards, we may conclude that for **Ib**, the molecular weights of PHEMA coincided well with the estimated values, meaning there was a better controlled polymerization [9].

Polymerization rates in water mediated by **Ia** and **Ib** increased dramatically in comparison with polymerizations carried out in acetone and MeOH despite ten degree lower temperature:40 °C in water vs 50°C in MeOH & acetone, but the control was very poor. The results of the polymerizations catalyzed by **Ia** in MeOH/water mixtures are shown in Table 1. Meanwhile the data for the water polymerizations catalyzed by different amounts of **Ib** are shown in Table 2.

**Table 1.** Polymerizations of HEMA in methanol, water/methanol mixtures containing varying amounts of water at  $40^{\circ}$ C. [HEMA]<sub>0</sub>/[**Ia**]<sub>0</sub>/[EBiB]<sub>0</sub> = 200:1:1.

MeOH / H2O	Time	Conv.	Mn, GPC X 10-3	Mn, th X 10-3	PDI
(v/v)	(h)	(%)	(g/mol)	(g/mol)	
100/0	24	-	-	-	-
85/15	6	24	17.5	6.2	1.88
50/50	6	69	44.9	18.0	1.93
15/85	3	83	71.6	21.6	2.09
0/100	2	90	110.0	25.7	2.00

•							10 L 10 L
	Initial	molar	Time	Conv.	Mn, GPC X 10-3	Mn, th X 10-3	PDI
	ratio		(h)	(%)	(g/mol)	(g/mol)	
	200/1/1		3	87	56.4	22.6	1.86
	200/0.5/1	l	1	36	70.1	9.6	2.06
			3	93	69.4	24.1	2.49
	200/0.1/1	l	2	25	107.6	6.5	2.66
			6	84	114.6	21.8	2.61

The living nature of the polymerization was verified by the chain extension methodology.



**Figure 4.** GPC curves of PHEMA-Br macroinitiator and its chain-extended polymer obtained with **Ib** complex at 50°C (a) in methanol and (b) methanol/water mixture.

The GPC traces of the PHEMA macroinitiators and the chain-extended polymers obtained in

Meoh and MeOH/water mixture (80/20 v/v) are shown in Fig. 4a and 4b correspondingly.

## Conclusions

Cyclometalated cationic complexes Ia and Ib, differing by the type of anion only, were able to catalyze fast radical polymerization of HEMA. The reaction proceeded under very mild conditions and achieved high conversions The level of control was different and depended on the catalyst and the polymerization conditions. The polymerization was controllable in organic solvents with both complexes but the control was better with Ia. The importance nature of the counterion was demonstrated. The polymerization accelerated significantly in the aqueous medium but proceeded without control. High activity together with good stability shown by Ib in the aqua polymerization makes it a promising candidate for controlled polymerizations of hydrophilic monomers [9].

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# SYNTHESIS OF BLOCK COPOLYMER POLY(DIMETHYLSILOXANE-B-METHYLMETHACRYLATE) BY ANIONIC RING OPENING POLYMERIZATION AND ATRP

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## Abstract

Microfluidic device [1] also called "lab on chip", is a concept that integrates in a single device all the necessary components to allow activities such as: dosage of medicines by microdoses, micro chemical synthesis, or the microanalysis of complex reactions, all of them, with the smallest amount of sample and reagents. In the construction of such devices, it is important to consider the biocompatibility of materials where polymers such as poly(dimethylsilicone) (PDMS) and poly(acrylic) (PMMA) can be considered as a good option [2]. However it is necessary to prepare a material with good mechanical properties. Here, we report the synthesis of the copolymer poly(dimethylsilicone-b-methylmethacrylate) through the combination of anionic ring opening polymerization and atom transfer radical polymerization (ATRP). PDMS macroinitiator was obtained by anionic polymerization of hexamethyltrisiloxane (D3) initiated by butyllithium, the living polymer was then quenched with chlorodimethylsilane. Hydrosilylation of 2-Bromo-2methyl-allyl-propanoate, produces a poly(dimethylsilicone)-omega-functionalizated ATRP initiator with a 98% of functionalization calculated by 1H-NMR and well defined molar mass distribution. Copolymerization with methylmethacrylate using PMDETA, copper chloride (CuCl) and methylethylketone as solvent gives high yield of the block colpolymer poly(dimethylsiliconeb-methylmethacrylate). Macroinitiator and block copolymer were both characterized by NMR, GPC, FT-IR, and DSC.

## Introduction

A microfluidic device comprises a promising concept for the application of several pharmaceutical treatments in micro-doses, and other applications such as micro-reactors, microanalysis (also named "total analysis system",  $\mu$ TAS or lab on chip). Such type of chemical devices integrates all the components needed to perform a specific analysis in a single device. By this way, chemical synthesis or pharmaceuticals delivery with the minimum needed amount of sample and reagent can be possible. However, in the development of these devices it is important to consider the biocompatibility of materials.

One of the most versatile materials for the construction of devices for biological applications is the polydimethylsiloxane (PDMS) [3]. However, due to its elastomer character, the preparation of the micro canals, pipes or ducts to conduct fluids becomes a difficult scientific topic. To pursue this objective, materials with processability properties of the thermoplastic material and the biocompatibility and mechanical properties of the elastomer must be synthesized.

Methylmethacrylate is a polymer with good mechanical properties that can also be compatible with biological systems.

Block copolymers belongs to an interesting class of materials, with a well-defined composition and architecture. They have unique and suitable properties for a wide variety of applications; commercially, they are used for example, as elastomers thermoplastics, adhesives, or surfactants.

In general, block copolymers are prepared through a sequential polymerization of two different monomers, using the same polymerization technique. However, recently, several efforts have been performed to get block copolymers either by the combination of different polymerization techniques or functionalization of the ending group in a growing chain where this new group will be now capable of initiate the polymerization of a second monomer.

Living ionic polymerization methods, have been used for the synthesis of well-defined block copolymers, however these methods are highly sensitive to impurities and require strict reaction conditions. The available methods of controlled radical living polymerization (CRP) [4], offer the advantage of less demanding experimental conditions for the preparation of copolymers block, as well as other complex structures.

The more widely studied and promising methods of CRP techniques are polymerization mediated by nitroxides (NMP) [5], polymerization by reversible chain addition fragmentation transfer (RAFT) [6,7] and atom transfer radical polymerization (ATRP) [4, 8-10]. Acar and Matyjaszewski [11] reported the preparation of block copolymers using a combination of two different living techniques: anionic and ATRP.

Here we report the preparation of poly(dimethylsiloxane-b-methylmethacrylate) through the anionic polymerization of hexadimethyldisiloxane with the functionalization of the ending group with dimethylsilane. ATRP initiator was introduced at the end of the PDMS polymer chain by the employment of the hydrosylilation reaction. The block copolymer was obtained when the PDMS macroinitiator was polymerized with MMA by the ATRP methodology.

## Experimental

n-Butillitum (n-BuLi). Metallic lithium was washed several times with hexane, cutted in small pieces and placed into a three necked flask of 1 L equipped with condenser and addition funnel. Then, a small amount of sodium and 150mL of hexanes were added to the flask, followed by 27.18 g (0.29 moles) of chlorobutane (n-BuCl) which was added drop wise through the addition funnel. The temperature was fixed at  $0^{\circ}$ C using an iced bath for 4 to 5 hours. The n-BuLi solution was decanted and transfered to a clean and under inert atmosphere flask through a cannula under pressure of argon. Finally, the concentration was determined by the ASTM E233 - 90 technique.

Poly(dimethylsilyl) hidrosilyl omega functionalized (PDMS-Si-H). In a gloves box, 26.498 g (119.109 mmol) of hexamethyldisiloxane (D3) were placed into a Schlenk type flask fitted with a magnetic stirrer. 10 mL of THF and 20 mL of toluene were then added and the solution stirred until D3 was completely dissolved. Then 0.909 g (1,314 Mmol) mL of n-BuLi were added to the reaction mixture and kept reacting for 12 h in agitation at room temperature. Once the reaction

time was completed, 1.434 g (15.151 mmol) of dichlorodimethyl silane freshly distilled were added dropwise. The mixture was kept at room temperature overnight in argon atmosphere. Later, the solvents were distilled under vacuum, 1 mmHg at room temperature. Finally, the reaction mixture was filtered using a Schlenk type filter under inert atmosphere, leading to a non-colored polymer with 90% yield. 1H NMR (300 MHZ, CDCl3 (0% TMS))  $\delta$ : 4.72 (q, 1 H, Si-H), 1.33 (m, 4 H, CH3-CH2-CH2), 0.90 (t, 3 H, CH3-CH2), 0.57 m, 2 H (CH2-Si) 0.10 (s, 6 H, the PDMS methyl).

10.27 g (0.578 mmol) of PDMS-Si-H (Mn = 17775), 0.767 g (3.466 mmol) of allyl 2-bromo 2methylpropionate and 29 mL of toluene were placed in a Schlenk tube equipped with a magnetic stirrer. At the same time, in another Schlenk tube 2.0 mg of methyl naphtoquinone (1.16 x 10-5 mol) and 18.5 mL of toluene were placed, and a yellow homogeneous solution was obtained. To this solution, 56.36  $\mu$ L (5. 777 x 10-6 mol) of the Karstedt's reagent as catalyst were added. This solution was added to the solution contained in the previous Schlenk tube through a cannula at room temperature. The reaction is placed in an oil bath at 70°C +/-0.1°C for 24 hours. The solution was precipitated in 300 mL of methanol with vigorous agitation and purified by liquid column chromatography using neutral alumina. The product was obtained in a 93% yield 1 H NMR (300 MHz, CDCl3 (0% TMS))  $\delta$ : 4.15 (t, 2 H, O-CH2), 1.93 (s, 6 H, C (Br)-(CH3) 2), 1.70 m, 2 H (CH2-CH2-CH2-O) 1.40 m, 2 H (CH2-CH2-CH2-CH2) 1.33 (m, 4 H, CH3-CH2-CH2), 0.90 (t, 3 H, CH3-CH2), 0.57 m, 2 H (CH2-Si) 0.10 (s, 6 H, methyl group in the PDMS) ppm. Functionality was determined by the ratio of integration between the methyl isobutyrate at 1.93 ppm and the protons of the methyl group in the initiator n-butyl at 0. 90 ppm, yielding a 95%.

Block copolymerization: A mixture of 0.0717 g (0.5 eq, 02497 mmol) of CuBr, 0.0575 g (0.5 eq, 0.2497 mmol) of HMTETA, 10 g (200 eq, 99.80 mmol) of MMA in methylethylketone as solvent and 0.487 g (0.5 eq, 0.2497 mmol) of the prepared macroinitiator PDMDS-ATRP, were placed in a Schlenk tube previously evacuated. This mixture was degassed by several vacuum-criogenic cycles in liquid nitrogen. After this process, the tube was sealed and placed in an oil bath at  $75^{\circ}$ C. Once the reaction time was reached, the reacting mixture was withdrawn from the oil bath and its content dissolved in THF and precipitated in hexane. The polymer was then filtered and dried under vacuum.

## **Results and Discussion**

The strategy followed to obtain the thermoplastic elastomer PDMS-b-PMMA is through a macrointiator prepared from the funcionalization of polydimethylsiloxane at the end of the growing chain with a reactive group which is able of initiate a second polymerization reaction. Due to the chemical nature of the monomers, the first step was the anionic ring opening polymerization of D3 followed by the in situ functionalization by dimethylchloro silane. The PDMS-Si-H can be later modified with allyl 2-bromo-2-methylpropanoate by the Kardest reaction. By this way, the prepared macroinitiator contains a group capable of initiating an ATRP reaction.

The synthesis of this macroiniciador was achieved using a polymerization which started with the reaction of n-butyl lithium and D3 (molar ratio of 1:0.01) followed by the addition of an excess of chloro dimethylsilane (Scheme 1). The viscous solution obtained at the end of the reaction was distilled to remove the unreacted monomer, and filtered through a Schlenk type filter to eliminate the formed salt (LiCl). The resulting PDMS polymer is end functionalized with - Si-(CH3)2-H and the percent of functionalization was determined by comparing integration for the signals at 0.90

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ppm that corresponds to the resonance of methyl protons in butyl group from the initiator and the resonance of the hydrosylil proton at 4.72 ppm. According to this procedure, 95 % of functionality was calculated. The GPC analysis for the macroiniciador showed a 20,000 g/mol molecular weight and polydispersity of 1.2, indicating the living character of the polymerization.



Scheme 1. Polymerization of hexamethyldisiloxane with butyl lithium.

Once the intermediate was prepared by anionic polymerization, the reaction of hydrosilylation of the allyl 2-bromo-2-methylpropanoate employing the Karstedt's catalyst and the PDMS-Si-H polymer was accomplished. This reaction was used to produce a monofunctional macroiniciador which contains an ATRP initiator on its structure. Methyl naphtoquinone was used as catalyst for this reaction which was completed after 24 hours at 70°C in toluene. The 1H NMR and FTIR spectra of the reaction product, showed that the hydrosilyl group was completely consumed, as depicted by the disappearance of the Si-H resonance at 4.75 ppm in NMR and the stretching band at 2128 cm-1in FT-IR. A new band appears at 1736 cm-1 which corresponds to the stretch of the carbonyl group present in the propionate moiety. Additionally a triplet resonance (J=8Hz) at 4.18 ppm is now present, corresponding to the methylene protons near to the oxygen atom in the ester group. Taking into account the spectroscopic evidence, we assure the presence of the desired compound.



Scheme 2. Preparation of the PDMS macroinitiatior

ATRP polymerization is sensitive to the solvent polarity and could affect the structure of the metal complex, and the rate polymerization [12]. Zhang and Shubert [13] studied the effect of the solvent in the ATRP of MMA catalyzed with FeBr2/N-Alkyl-2-pyridilmethanimine as ligand; they found that the use of methyl ethyl ketone (MEK) gives greater polymerization rate and better control over the molecular weight in MMA homopolymerization. Therefore, MEK was used in the

following block copolymerization studies.

The reaction of copolymerization of MMA by ATRP was initiated with the PDMS-Br macroinitiator (MW = 20,381 g/mol, dispersity = 1.2) and catalyzed with CuBr, using pentamethyldiethylenetriamine (PMDETA) as ligand and MEK as a solvent at 75°C, in a molar ratio of MMA:PMDETA: CuBr:PDMS - Br / 200: 1: 1: 1. Molecular weight of the obtained copolymer was 28,256 g/mol, with PD = 1.3 and initiation factor (f) of 0.8, defined as the ratio between expected molecular weight divided by the experimental molecular weight of the copolymer. This data is important and can be considered as a measure of the control of the copolymerization reaction.



Scheme 3. Preparation of the block copolymer poly(dimethylsiloxane-b-methylmethacrylate) by ATRP.

Characterization of the block copolymer was conducted by analytical methods. Differential scanning calorimetry confirms the synthesis of the block copolymer by the presence of two glass transition temperatures; one of them located at 229 K and corresponding to the transition of the block of polydimethylsiloxane. The other one at 393 K belongs to the polymethylmethacrylate block. The infrared spectrum shows a characteristic signal for the stretch of the carbonyl group on the methacrylate group at 1736 cm-1 and the stretch for the C-O bond of the methoxy group at 1020 cm-1. The copolymer also presents the signals corresponding to the stretch of Si-O and SiCH3 in 1096 and 811 cm-1 respectively.



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Scheme 4. FTIR spectrum of the block copolymer poly(dimethylsiloxane-b-methylmethacrylate).

NMR analysis was used to determine the copolymer composition of the two monomers, relating the integration for each proton from the resonance of 3 protons of the methoxy group at 3.60 ppm (Hm), with the integration of each proton for the 6 protons of the two methyl groups attached to the silicon atom in the polydimethylsiloxane which has resonance at 0.1 ppm. According to this analysis, the composition of the block copolymer corresponds to 42% w/w for methylmethacrylate and 58% w/w for dimethylsiloxane.

## Conclusions

The macroinitiator of PDMS omega functionalized with the group 2-bromo-2-methyl propionate (PDMS-Br) which is able to initiate a copolymerization with acrylic monomers was prepared. The strategy of synthesis starts with the anionic ring opening polymerization of hexadimethyldisiloxane, subsequent transformation by the hydrosylilation reaction. The brominated polymer was obtained with high percent of functionality (92%). This new polymer was used to initiate the copolymerization of methylmethacrylate by ATRP. The polymerization process was conducted with well controlled behavior.

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# SYNTHESIS OF BROMINATED POLYSTYRENE USED AS MACROINITIATOR FOR ATRP

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#### Abstract

The macroinitiators of brominated polystyrene (mPS-Br) were synthesized using N-Bromosuccinimide (NBS) and azobis-isobutyronitrile (AIBN) with different molar ratios, at 120°C and reaction time of 3h. Macroinitiators with varying bromine content were obtained, these brominated species can be used as macroinitiators in the preparation of graft or block copolymers.. The used polystyrene is atactic with a molecular weight (Mn) of 81000 g/mol and molecular weight distribution (Mw/Mn) of 1,8. Under these reaction conditions, the brominated polystyrenes were obtained with yields ranging from 50-98%. The analysis by GPC determined that the macroinitiators mPS-Br displayed a reduction of the Mn. The macroinitiators obtained with greater molar ratio [NBS]/[AIBN] displayed the lowest Mn, and the molecular weight distribution did not undergo great changes. Graft polymerization technique with CuBr/N,N,N,N,N-pentamethyl diethylenetriamine. The high reaction rate was obtained for graft copolymerization when high concentration of macroinitiator mPS-Br was used, favoring the gel formation. The versatility of the graft copolymerization was evaluated when a set of polymers were prepared with different quantities of MMA these materials were analyzed with NMR spectroscopy. In absence of macroinitiators mPS-Br, under identical ATRP reaction conditions, PMMA was not produced.

#### Introduction

Controlled radical polymerization techniques (CRP) can offer the possibility of preparation of new materials that can be used for different applications. One of them are the graft copolymers which are a typical examples of materials that has application in the field of high impact materials, thermoplastics elastomers, surface modifiers, polymeric emulsifiers, among others.

Atom transfer radical polymerization (ATRP) is CRP technique which has a great versatility in the preparation of graft polymers with a variety of functionalized monomers, and allows polymerization at high impurity levels. Particularly, ATRP is insensitive to oxygen traces, which are quickly removed by the oxidation of the ATRP catalyst. Most typical ATRP catalytic systems are commercially available, and can be used as acquired without modifications, for practical uses [1,2]. ATRP technique exhibits a rapid and reversible equilibrium process between dormant and growing species.

The main feature of the ARTP is the reversible consumption of highly active free radicals driving to a dormant species that can be reactivated to free radical, controlling the propagation step and decreasing the possibility of the termination through recombination or disproportionation. The controlled polymerization conditions arrives from the magnitude of the activation-deactivation equilibrium showed on the Figure 1.



Figure 1. ATRP mechanism

The use of styrenic polymers as macroinitiators in the synthesis of copolymers through controlled polymerization techniques, has been widely studied. Most of the reports are related to the grafting onto the phenyl group, and just a few of them deal about the formation of block copolymers. [3-8] Our research group is interested in studying the synthesis of new polymers using different polymerization techniques. Recently, we report the first results related to the synthesis of copolymers based on styrene (S) and methylmethacrylate (MMA) using macroinitiators based on bromine functionalized polystyrenes (PS), through ATRP technique. This polymerization method allowed us to obtain block copolymers with different MMA contents. Macroinitiators were synthesized *in situ*, after syndiotactic styrene polymerization in presence of elemental bromine. [9].

Here we report the synthesis of graft copolymers PS-g-PMMA, using ATRP technique and brominated macroinitiators. Bromined PS macroinitiators (mPS-Br) were prepared with the reaction of PS, N-Bromo succinimide (NBS) and isobutyronitrile (AIBN) at different [NBS]/[AIBN] molar ratios at 120°C, for 3 h The grafted PMMA chains were detected on the PS main chain

#### Experimental

A glacial acetic acid solution of cupper bromide I (Cu(I)Br, Aldrich 98%) was stirred under inert atmosphere during 24 hrs. The mixture was degasified by several freezing-nitrogen cycles, filtered through a glass frit filter and then washed with acetic acid, ethanol and ethylic ether. After this procedure, Cu(I)Br was dried at  $40^{\circ}$ C for three days under reduced pressure (2mm Hg), and then the solid was storage under inert atmosphere.

N,N,N',N'',N''-Pentamethyldiethylentetramine (PMDETA, Aldrich), Trichlorobenzene (TEDIA, HPLC spectra), Acetone (J.T. Baker 99%), Hexane (J.T. Baker 99%) and Tetrahydrofurane (Aldrich CHROMASOLV for HPLC 99.9% inhibitor free) are used with out purification. Methylmethacrylate (Aldrich 99%) was purified with magnesium sulphate under inert atmosphere, and distilled at 60-67°C under reduced pressure of 2 mm Hg. 2,2-azo-*bis*-isobutyrenitrile (AIBN) was re-crystalized in diethylether at -10°C. N-Bromine Succinimide (NBS) was dissolved in 300 mL of boiling water. Next, the water solution was cooled at 5°C for 48 h. filtered and dried in vacuum.

## Synthesis of Macroinitiator M20

A solution of Polystyrene (0.048 mol, Mn = 81000 g/mol, Mn/Mw = 1.8) in 50 mL of

Trichlorobenzene was added at 120°C 0.0235 mol of NBS and 0.00304 mol of AIBN under inert atmosphere. The mixture was stirred for 180 min, after de stipulated time the reaction, was warmed at room temperature and spilt in a glass of precipitates with hexane, the precipitated polymer was washed with acetone in order to eliminate the NBS that did not react. The polymer was washed again with hexane and dried under vacuum at room temperature for 8h, the yield was 51.8 %, the molecular weight, Mn = 10658 g/mol and polydispersity, Mn/Mw = 1.8.

## Synthesis of copolymer PS-g-PMMA<sub>(22)</sub>

The copolymers were synthesized following ATRP's normal procedure.  $9.36*10^{-4}$  mol of CuBr ,  $9.36*10^{-4}$  mol PMDETA, 0.147 mol of methylmethacrylate and  $9.38*10^{-6}$  mol of macroinitiator mPS-Br. were added to Schlenk flask under inert atmosphere. Then the mixture was allowed to stir at a temperature of 30°C for 20 min. After this time, the resulting mixture was precipitated using an excess of methanol, the graft copolymer was filtered and dried under vacuum for 5h, the yield was 2.1%, the molecular weight Mn = 20162 g/mol and polydispersity Mn/Mw = 4.7.

## **Characterization Methods**

Molecular weight (MW) and molecular weight distributions (MWD) for macroinitiators and copolymers were determined by gel permeation chromatography technique (GPC) at low temperature, using a GPC Hewlett Packard serie 1100, coupled to a PL GEL column, Mixta 1K-4M and 400 K-40M 10 6 A<sup>o</sup> with index refraction detector using polystyrene standards, and THF (Aldrich CHROMOSOLV for HPLC 99%) 1 mL/min as flow solvent, at 40°C. Proton NMR spectra, were determined in a Nuclear Magnetic Resonance equipment, JEOL 300 MHz FT NMR spectrometer Eclipse 300, using CDCl<sub>3</sub> as solvent. Thermal analyses were evaluated by scanning differential calorimetry, in a DSC 2920 modulated DSC, TA Instruments equipment with a heating ramp of 10°/min from 0 – 280°C under 50 mL/min flow of UAP nitrogen. FTIR spectra were determined using a Nicolet FT-IR Magna 550 spectrometer, provided with a KBr optical interpherometer, which operation range between 7000 – 30 cm<sup>-1</sup> has a 0.5 cm<sup>-1</sup> of resolution.

## **Results and Discussion**

Usually low molecular weight alkyl halides (RX) are used as initiators for ATRP reactions, compared to other alkyl halides, for example if we compared the use of the three halogens, bromine is most utilized by far, due to its lower bond energy dissociation (C-Br)[10]. The use of telequelic polymers containing C-Br terminal functionalities, has been less reported, compared to functionalized polymers with bromine atoms distributed along the polymeric chain, where is possible to graft other polymer chains.

In a previous work we reported the use of telequelic polystyrenes, with bromine terminal chains as initiators for ATRP polymerizations. In the present work we are reporting the use of polybrominated polystyrene (mPS-Br) which contains bromide along the polymeric chains, for evaluation as macroinitiators in ATRP reactions. The mPS-Br was synthezised from atactic PS and NBS, using AIBN as initiator, as represented in Figure 2.



Figure 2. Synthesis of bromided Polystyrene

Polystyrene used for the synthesis of mPS-Br macroinitiators was obtained from radical polymerizations, with molar mass of Mn = 81,000 g/mol and polydispersity of Mw/Mn= 1.8, determined by GPC.

Polystyrene bromination reaction was conducted at high temperature (120°C), using trichlorobenzene as solvent. At these conditions, interactions between PS and NBS/AIBN showed a rapid gas generation, which suggested that bromination reactions were taking place, and the homogeneous solutions were reacting for 3 hrs. NBS/AIBN molar ratios of 7.7 and 1.9 were used for bromine functionalization reactions, and Table 1 summarizes the results obtained for both experiments.

Exp.	PS	NBS	AIBN	$Y(\%)^a$	Mn <sup>b</sup>	$(Mw/Mn)^b$
	mol	mol	mol			
20	0.048	$2.35*10^{-2}$	$3.04*10^{-3}$	51.8	10658	1.8
28	0.048	5.89*10 <sup>-3</sup>	$3.04*10^{-3}$	98	45507	2.2

Table 1.- Functionalization conditions and results of bromination reactions

a) Gravimetric method b) GPC analysis, polystyrene standards

Experiment 20 corresponds to the PS functionalization reaction carried out at higher concentration of NBS/AIBN (7.7 mol). The functionalized mPS-Br was obtained in yields of 51.8%. Macroinitiator **M20** showed Mn = 10,658 g/mol, lower than the Mn of the initial PS, which suggests that the strong reaction conditions (NBS/AIBN ratio) could provoke fragmentations of the C-C bonds, on the starting PS. On the other side, the use of lower NBS/AIBN ratios led to higher yields and molecular weights of the macroinitiator **M28** (98 % and Mn= 45 507 g/mol respectively). Bromine functionalization of PS decreased its molar mass, close to the NBS/AIBN ratio used during the functionalization reaction. As for polydispersity values, there was no significant changes observed for the Mw/Mn of the new macroinitiators, which could represent an advantage for this functionalization method, since ATRP macroinitiators of low molecular weight and narrow molecular weight distributions are desirables for obtaining block copolymers. Macroinitiators (mPS-Br) **M20** and **M28** were also characterized by elemental analysis, and these results are showed in Table 2.

|--|

Macroinitiator	%C	%H	%Br <sup>a</sup>
M20	87.64	6.86	5.50
M28	80.81	6.70	12.49

a)Calculated as complement to 100%

In terms of Br mol % of functionalization, PS was modified at 5.5 and 12.5 mol % for **M20** and **M28** respectively. The highest bromide incorporation was achieved using a NBS/AIBN ratio of 1.9, where several experimental evidences suggested that high NBS/AIBN ratios favour the rupture of C-C bonds over the bromation reaction in the polymeric chains.

Macroinitiators characterization by FTIR showed evidences about the bromation sites in the PS. FTIR spectra show strong bands at 699 cm<sup>-1</sup> corresponding to *para* hydrogen of the aromatic group, and other stretching band at 539 cm<sup>-1</sup> was observed for the C-Br bond.

The <sup>1</sup>H NMR analysis of macroinitiators mPS-Br also showed evidences of functionalization along the polymeric chain (Figure3). Signal integration of aliphatic protons is lower than expected, comparing to that of aromatic protons. This suggests that bromation was carried out along the main polymeric chain. <sup>1</sup>H NMR spectrum displayed signals corresponding to PS and two new signals. Resonance at 1.5 ppm is due to CH<sub>2</sub> protons from the main polymeric chain, adjacent to C-Br bonds. Signal at 3.75 ppm corresponds to the typical chemical shift of CH-Br, which can also account as an evidence of bromation of CH<sub>2</sub> groups along the PS chains. Chemical shifts for other CH<sub>2</sub> brominated polymers, have been reported between 3.3-3.9 ppm [11], however, in order to confirm the above for this PS functionalization, a more detailed study for the macroinitiator structures mPS-Br was carried out.



Figure 3. 1H NMR spectrum of Macroinitiator M20

Functionalized polystyrenes (mPS-Br) were evaluated as macroinitiators in the polymerization of MMA, through ATRP at room temperature, for avoiding chain transfer reactions. Higher molar ratios of CuBr/mPS-Br than used in conventional ATRP reactions were used in these polymerizations, because the macroinitiators contain more than one active site (Figure 4). In addition, copolymerizations were carried out in bulk, using different amounts of MMA. Table 3 shows copolymerization reaction results using **M20** macroinitiator.



Figure 4. MMA copolymerization with functionalized polystyrene by ATRP

Experiment G21 was conducted at the highest M20 and MMA concentration utilized in these reactions, using a molar ratio of CrBr/M20 = 14. During the first 20 minutes of reaction, an increase in the solution viscosity was clearly observed, and at 45 minutes gel formation prevented agitation of the mixture, ending the copolymerization reaction.

Grafted copolymer (PS-g-PMMA) yield was of 36.6 wt % and the insoluble part was quantified as 31 wt %. Soluble polymer was characterized by GPC, showing Mn = 12,861 g/mol and MW/Mn = 4.5. The gel formation was attributed to the radical-radical coupling reactions between macroinitiator molecules, which are functionalized along the polymeric chains.

Exp	R.T. (min)	[a-PS-Br] mol	[CuBr] Mol	MMA mol	Y (%) <sup>a</sup>	Mn <sup>b</sup>	(Mw/Mn) <sup>b</sup>
CO1 6	4.5	0.00+10-5	1.04+10-3	0.1700	26.6	10061	4.5
G21 °	45	9.38*10	$1.34*10^{\circ}$	0.1782	36.6	12861	4.5
G22	20	9.38*10 <sup>-6</sup>	$9.36*10^{-4}$	0.147	2.1	20162	4.7
G23	20	9.38*10 <sup>-6</sup>	9.36*10 <sup>-4</sup>	0.135	0.74	18473	3.1
G25 <sup>d</sup>	20	9.38*10 <sup>-6</sup>	$1.35*10^{-3}$	0.217	1.5	981798	1.4
G30 <sup>e</sup>	50	9.38*10 <sup>-6</sup>	$1.7*10^{-4}$	0.023	7.2	1220538	1.2

Table 3.- MMA copolymerization results using macroinitiator M20

a) gravimetric method; b) GPC analysis, polystyrene standards; c) 31 wt .% gel d) Mn=14421 g/mol y (Mw/Mn) 3.7 e) Mn= 22832 (Mw/Mn) = 2.6

In order to get a better MMA graft copolymerization control, experiment G30 was carried out at low **M20** concentration, where gel formation was not observed, even after 50 minutes of reaction. However the GPC analysis of the PS-g-PMMA displayed two curves on its chromatogram, suggesting bimodal distributions for the grafted copolymers. Molar mass data of these copolymers are showed in Table 2.

It is important to note that MMA homopolymerization is not detected in the copolymerization reactions, since at these conditions, MMA was not polymerized in the absence of the macroinitiator mPSBr.

Polymerizations carried out using  $9.38*10^{-6}$  moles of macroinitiator **M20** and molar ratios of Cu/**M20** higher than 14, correspond to G22 and G23 experiments (Table 3). For both G22 and G23 experiments, the use of Cu/**M20** = 100 and 20 minutes of reaction time, led to the production

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of PS-g-PMMA in 2.1 and 0.74% yields respectively, no gel formation was detected, and their GPC chromatograms showed a broad monomodal curve of wide molar mass distributions.

As for G25 experiment, a higher ratio Cu/M20 = 144 and 20 minutes of reaction time were used, in order to favor the free radical generation for production of the grafted copolymer, however the yield of the copolymer did not increase significantly, and as in the above reactions, a bimodal distribution of molecular weights was observed. According to these observations, it appears that beside the grafting MMA reaction, coupling reactions between macroinitiator chains are also taking place. Macroinitiator coupling reactions increases as the reaction progress, until gel formation.

In order to probe the above, experiment G21, which produced 6.6 yield % of Ps-g-PMMA and 31 wt.% gel, was reproduced at shorter reaction times of 20 min. Under these copolymerization conditions, 14 yield % of the grafted copolymer was observed, without gel formation in the copolymer. GPC analysis of the grafted copolymer, showed bimodal molecular weight distributions.

Grafting copolymerization reactions of MMA and the **M28** macroinitiator (Mn = 45,507 g/mol and 12.49 mol % of bromide) showed similar results, compared to that obtained for **M20** macroinitiator, using concentrations between  $2.1*10^{-5}$ -  $2.9*10^{-6}$  M (See Table 4). At these copolymerization conditions gel formation was avoided, while the conversion increased for the reaction, however bimodal molecular weight distributions were also observed for the materials. The GPC curves of the copolymers PS-g-PMMA<sub>(34-38)</sub> are shown in Figure 5.

Exp	R.T.	[a-PS-Br]	[CuBr]	Y(%) <sup>a</sup>	Mn <sup>b</sup>	(Mw/Mn) <sup>b</sup>	Mn	Mw/Mn
	(min)	mol	mol					
G31	20	$2.9*10^{-6}$	$2.77*10^{-4}$	4.6	972598	1.4	18450	2.2
G34	20	$2.15*10^{-6}$	3.10*10 <sup>-3</sup>	5.7	868723	1.5	15323	2.0
G35	20	$2.16*10^{-6}$	8.6210 <sup>-6</sup>	6.4	792675	1.5	7378	1.6
G37	20	$2.77*10^{-5}$	$1.38*10^{-4}$	6.24	812619	1.5	8238	1.6
G38	120	$2.77*10^{-5}$	$3.6*10^{-4}$	5.1	776578	1.4	36417	2.1

 Table 4.- MMA Grafting copolymerization results using M28

[MMA= 0.049 moles]; a) gravimetric method; b) GPC polystyrene standards



Figure 5.- GPC curves of copolymers prepared with macroinitiator M28

This method for preparation of PS-g-PMMA copolymers from mPS-Br macroinitiators, shows special features for producing bimodal copolymers, combining high molecular weight chains (>  $7*10^5$ ) with other types of low molecular weight fragments, representing an advantage because its usefulness as additive for improving processability for different polymeric materials. Figure 6 shows a scheme reaction, about the formation of high molecular PS-g-PMMA.



Radical-Radical coupling

Figure 6.- Schematically representation of high molecular weight PS-g-PMMA formation

Chemical structure and molar ratio of PS and PMMA, were determined by <sup>1</sup>H NMR analysis of the copolymers PS-g-PMMA, (Figure 7). <sup>1</sup>H NMR spectrum of PS-g-PMMA showed characteristic signals for PS and PMMA segments, whose mol % contents were determined by integration of the aromatic protons and the methyl group of O-CH<sub>3</sub>, for PS and PMMA, respectively. All copolymers showed high mol % of MMA incorporations, where the lowest

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MMA content was calculated about 35mol % for PS-g-PMMA<sub>(22)</sub>.



Figure 7. - 1H NMR spectrum of PS-g-PMMA(22)

#### Conclusions

The use of brominated polystyrene macroinitiators in ATRP copolymerizations, was found to be useful in obtaining a successful method for producing grafted copolymers PS-g-PMMA. A careful selection of the copolymerization parameters prevents gel formation during the copolymerization process, forming bimodal PS-g-PMMA copolymers, which can be useful as processing improver additives.

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## FACILE FUNCTIONALIZATION OF SUBSTRATES WITH TEMPO USING OXOAMMONIUM SALTS

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Nitroxides are stable free radicals that in the presence of a specific counter-ion could lead to oxoammoniumsalts (OS).[1] This kind of salts are powerful, selective, and nonmetallic oxidants extensively used for the oxidation of primary and secondary alcohols to aldehydes and ketones, respectively.[2] However, we have found that the OS are not only excellent oxidant agents but that, in the presence of a base (e.g., triethylamine, Et3N), its chemistry of oxidation radically changes to a chemistry of functionalization, which is not an obvious result.[3] Thus, on this basis, in principle practically any substrate, molecule, or chemical compound containing hydroxyl groups could be functionalized with nitroxide moieties using OS in only one step.

In the present work I will show you some examples of the functionalization of different polymeric substrates and nanoparticles with TEMPO groups in a only one step using SO. In the first part of the talk, I will disclose how the polymers hydroxy-terminated can be functionalized by TEMPO and their use to extend the chain in order to obtain block copolymers amphiphilos. In the second part, the functionalization of nanoparticles of SiO2 and TiO2 will be demonstrated as well as, their use as hybrids alkoxyamines in the synthesis of grafting of PSt controlled by TEMPO. Also in the case of TiO2 their functionalization with TEMPO groups, will be demonstrated using theoretical analysis (Density Functional Theory and B3LYP)

The use of SO is a route recently proposed by our group to obtain substrates functionalized with TEMPO under mild conditions[4].

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## SYNTHESIS OF STIMULI-RESPONSIVE, WATER-SOLUBLE POLY[(DIMETHYLAMINO)ETHYL METHACRYLATE/STYRENE] STATISTICAL COPOLYMERS BY NITROXIDE MEDIATED POLYMERIZATION

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Polymers that have sharp and reversible responses to stimuli such as changes in temperature are known as "smart" materials. Consequently, water-soluble "smart" polymers are widely studied for applications towards sensors and biomedical materials. Poly(dimethylamino)ethyl methacrylate (PDMAEMA) is a water-soluble polymer that is responsive to both temperature and pH changes. To precisely control the properties of such a polymer, controlled radical polymerization (CRP) techniques have been used. As one of the CRP techniques, nitroxide-mediated polymerization (NMP) does not involve any metal-containing catalysts or sulfur-based agents that other CRPs may require, making it potentially advantageous for synthesis of non-cytotoxic polymers for biomedical applications [1]. However, homopolymerizations of methacrylates for NMP generally associate with very high equilibrium constants which lead to an excessively high radical concentration that promotes self-termination [2]. In this study, DMAEMA was statistically copolymerized with 5-20mol% styrene as the controlling co-monomer at 80 °C in bulk using a unimolecular alkoxyamine initiator called BlocBuilder functionalized with a N-hydroxysuccinimidyl (NHS) ester end group (NHS-BlocBuilder). The detailed results concerning the NMP synthesis of DMAEMA-rich copolymerizations (kinetics, level of control and livingness of the copolymers) will be presented. Also, the influences of copolymer composition, solution concentration as well as polymer microstrucutre on the responses of the copolymers to temperature and pH changes in aqueous media were examined by dynamic light scattering and UV-Visible spectrometry. The combination of NHS-BlocBuilder with DMAEMA-rich feeds enabled the development of water-soluble "smart" polymers that could also later be conjugated to biological compounds or other amine-containing materials.

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# CHITOSAN MODIFICATION WITH GRAFT COPOLYMERS BY A GREEN PROCESS

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#### Abstract

The synthesis and characterization of chitosan-g-poly(styrene-maleic anhydride)-OH-TEMPO (CTS-g-PSMA-OH-T) are reported. The chitosan chemical modification with diverse groups in specific sites of the molecule results in a biodegradable and human body biocompatible material which has potential application in the medicine field for controlled drug delivery systems. In the first step of the procedure the bromine 4-OH-TEMPO oxoammonium salt is synthesized according to Bonilla-Cruz et. al. The salt is totally soluble in aqueous media. In the second step, a chitosan functionalization reaction was carried out from the previously synthesized salt in aqueous acid solution containing 0.1 M acetic acid in the presence of triethylamine. The success of the reaction was demostrated by 13C RMN CP MAS, and TGA. A yield of 18.9 % of functionalized OH's on the chitosan backbone is achieved. Finally graft copolymerization of styrene and maleic anhydride was performed via NMRP by an unimolecular initiation system in which the functionalized chitosan acts at the same time as a macroinitiatior and controller. The reaction was performed by dispersion in supercritical carbon dioxide (scCO<sub>2</sub>) in the presence of camphorsulfonic acid (CSA) in order to avoid the autocopolymerization of the monomers. From 13C RMN CP MAS, and TGA tests the synthesis of the CTS-g-PSMA-OH-T is evidenced.

#### Introduction

Chitosan (CTS) is a biopolymer industrially produced by the alkaline N-deacetylation of chitin, a polysaccharide present in most crustacean shells and insects. The structure of CTS is composed of 2-amino-2-deoxy-D-glucopyranose  $\beta(1\rightarrow 4)$ -links and to 2-acetamido-2-deoxy-D to glucopyranose[1]. When the degree of deacetylation of chitin reaches about 50%, it becomes soluble in aqueous acidic media and is called chitosan. The solubilization occurs by protonation of the -NH2 function on the C-2 position of the D-glucosamine repeating unit, whereby the polysaccharide is converted to a polyelectrolyte in acidic media [1]. Chitosan is the only pseudonatural cationic polymer and therefore, it finds many applications in the medical, food, industrial and agricultural fields and it is a very attractive material due to its good biocompatibility with the human body [2-3]. In order to obtain advanced materials derived from CTS; this biopolymer has been subjected to chemical modifications like controlled incorporation of substitutes in specific positions of the molecule [4]. In this research we describe the chitosan modification by the incorporation of the graft copolymer of styrene-maleic anhydride (SMA) using the "Nitroxide Mediated Radical Polymerization" (NMRP) from a previous CTS functionalization reaction with TEMPO groups. The functionalization reaction was carried out in acid aqueous environment in the presence of a type of oxoammonium salt; identified as Br-OH-TEMPO salt (previously synthesized) and triethylamine, according to Bonilla-Cruz et. al. [5]. The copolymerization reaction was carried out in supercritical carbon dioxide (scCO<sub>2</sub>) as reaction media in the presence of the functionalized chitosan, styrene, maleic anhydride, and camphor sulfonic acid in order to avoid the auto-copolymerization of the monomers [6]. ScCO<sub>2</sub> is considered a flammable, inert, low-cost, low toxicity, and high purity solvent [7].

## Experimental

#### Synthesis of Br-OH-TEMPO oxoammonium salt

The synthesis of Br-OH-TEMPO oxoammonium salt (1-Oxoammonium-4-hydroxy-2,2,6,6-tetramethylpiperidinium bromide) (Figure 1) was reported previously by Bonilla-Cruz et. al.[5]. In a typical experiment, bromine (0.032 mol) was slowly added to a solution of 4-OH- TEMPO (0.032 mol in 100 mL of CCl<sub>4</sub>). A brown solid was formed almost instantaneously and was separated from the solution by filtration. A small amount of additional bromine was added to obtain more salt of Br-OH-TEMPO thus improving the reaction yield (90%). The filtrate was exhaustively washed with CCl<sub>4</sub> until the filtered solution showed no anymore color. The Br-OH-TEMPO salt was dried over vacuum at 40 °C for 24 h.



Figure 1. Schematic illustration of synthesis of Br-OH-TEMPO salt

#### Chitosan functionalization reaction

First, 0.5 gr of chitosan were dissolved in 100 mL of acetic acid 0.1M in a glass reactor. In the second step the solution was stirred for 1 h and then 0.0049 mol of TEA was added and immediately 0.0042 mol of the Br-OH-TEMPO oxoammonium salt (dissolved in 40 mL of 0.1M acetic acid) was added. Finally the reaction system was saturated with inert argon atmosphere and stirred for 48 h at room temperature. After that, in order to remove the residual Br-OH-TEMPO oxoammonium salt the functionalized chitosan was purified four times by precipitation in acetone and re-dissolution in acetic acid 0.1 M. Then the Chitosan-TEMPO (CTS-T) was lyophilized for 24 h. The CTS and CTS-T were analyzed by 13C NMR CP-MAS and TGA. In order to retrieve the triethylamine salt, which is the byproduct formed during the reaction, the acetone solution (which was used to precipitate the chitosan) was subjected to precipitation in tetrahydrofuran (THF). This salt was filtered and lyophilized for 12 h. Because the reaction was carried out in an acidic media, the pH was measured throughout the functionalization reaction in order to maintain the acidic character.

## Graft copolymerization on scCO<sub>2</sub>

The copolymerization of styrene-maleic anhydride was conducted in a 25 mL stainless steel reactor. The copolymerization was carried out as follows: CTS-T (0.15 gr), styrene (10 mL, 9.04 g, 0.087 mol), maleic-anhydride (0.44 g, 0.0045 mol), CSA (0.37 g, 0.0016 mol), and a magnetic stirrer were added to the reactor. Subsequently, the reactor was pressurized with  $CO_2$  up to 18.96 MPa. Afterwards, the reactor temperature was raised to 130 °C using a heating mantle. After five hours of reaction, the polymerization was stopped by cooling the reactor with iced water, and the  $CO_2$  was slowly evaporated. The polymer was precipitated in methanol in order to remove remaining styrene and maleic anhydride. In order to remove the CSA from the CTS-g-PSMA-OH-T, the product was precipitated in water, where the CSA was dissolve and the CTS-g-PSMA-OH-T precipitated. The CTS-g-PSMA-OH-T was lyophilized 24 h and finally analyzed by 13C-NMR CP-MAS and TGA.



Figure 2. Schematic illustration of the functionalization reaction and graft copolymerizationon

#### **Results and Discussions**

The Br-OH-T oxoammonium salt synthesized is stable and totally soluble in an aqueous medium. The proposed functionalization reaction mechanism is discussed by Bonilla et. al. [5] There is still some debate about the correct structure of the intermediate 2 specifically regarding the nature of the bond between the CTS and the TEMPO moety. In the functionalization reaction, 0.59 mmol out of a total of 3.1 mmol of OH groups were functionalized with a total of 3.1 mmol possible hydroxyl groups, equivalent to 18.9% (determined according to the recovered triethylamine salt). The yield of the graft copolymerization reaction as a function of chitosan with graft copolymers chains out of the total was 76%, the monomer conversion was 2.6%; from this conversion and the nitroxide molar concentration present in the 0.15 g of CTS-T, we estimated the Mn of the graft chains on 1640 g/mol. It was not possible to determine a molecular weight distribution, and therefore the control level of the graft polymerization due to poor solubility of chitosan-based materials in common organic solvents.

#### Thermogravimetric analysis

The figure 3a corresponds to CTS. This figure revels a first loss (2.88 wt.-%) which is mainly attributed to the loss of physisorbed water. After the first temperature ramp (5 °C/min), when the temperature reached 70°C, a temperature plateau was maintained for 30 min in order to eliminate the largest possible amount of physisorbed water. The second loss, at 200 °C, corresponds to the pyrolysis of the biopolymer, which begins with the division of the glycosidic bonds followed by the degradation of chitosan [4]. The figure 3b corresponds to CTS-T, this thermogram shows the weight loss of water physically absorbed in the range of 30 °C to 100 °C. After that, a positive change in the slope of the derivative curve occurs, that reaches a local maximum value at 126 °C. This value is attributed to the rupture of the bond between the chitosan and the nitroxide. The weight loss in this interval (1.85 wt.-%), suggests the removal of 4-OH-TEMPO, since this kind of nitroxide is known to exhibit high volatility with a trend to sublimation under relatively mild conditions of pressure and temperature [5]. Figure 3c (CTS-g-PSMA-OH-T) shows a first weight loss (2.04wt.-%) attributed to water physically absorbed. Also it is shown a positive change in the slope of the curve at 178.04 °C, mainly attributed to the separation of the copolymer from the chitosan and/or to the ring opening of maleic anhydride present in the SMA. At 373.45 °C a



weight loss due to the complete degradation of the material is shown [5].

Figure 3. TGA analysis of a) CTS, b) CTS-T, and c) CTS-g-PSMA-OH-T

## Nuclear magnetic resonance in solid state

The experiments of 13C NMR CP-MAS were carried out in a FT-NMR Bruker Avance spectrometer of 500 MHz and 18000 scans of resolution. The CTS spectrum (figure 4a, black line) shows at 108.4 ppm the chemical shift corresponding to C1, at 61.26 that of C2, and at 65.13 ppm that of C6. The displacements of C3 and C5 overlap at 79.32 ppm. With respect to the resonance of C4, two signals are in the range of 86.39 to 89.27 ppm, these signals can be separated due to differences in arrangement of the polymer chains and also different torsion angles [8]. The CTS-T spectrum exhibits, besides the signals corresponding to CTS, a new chemical shift at 36.52 ppm corresponding to the four carbons of the methyls of TEMPO (C10, C11, C16 and C17). The secondary carbon resonances of the nitroxide (C12 and C14) appear at 50 ppm.

The CTS-g-PSMA-OH-T spectrum (figure 4b) shows, besides the signals of CTS, the displacements corresponding to styrene units at 127 ppm assigned to carbons S4, S5, S6, S7 and S8 of the benzene ring. S3 is observed at 144 ppm. The carbons  $\alpha$  y  $\beta$  to the aromatic ring (S1 and S2 respectively) are shifted by 40 ppm. The carbonyl groups (A2 and A3) of the maleic anhydride units are shifted at 173 ppm, and the carbons A1 and A4 are asigned at 51 ppm.



Figure 4. 13C NMR CP/MAS analysis of a) CTS, CTS-T and b) CTS-g-PSMA-OH-T

#### Conclusions

The graft copolymerization of styrene-maleic anhydride on CTS was carried out by NMRP via an unimolecular initiation system using  $scCO_2$  as reaction media starting from a previously formed TEMPO functionalized CTS (CTS-T). The CTS-T acts as macroinitiator and controller at the same time, and this material it is considered a precursor of hybrid materials with controlled graft polymers. Performing the graft copolymerization in  $scCO_2$ , in adition to being kind to the environment, provides an advantageous alternative with respect to the use of organic solvents, preventing subsequent purification processes of the product.

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## TEMPO MEDIATED RADICAL EMULSION POLYMERIZATION OF STYRENE BY STEPWISE AND SEMIBATCH PROCESSES

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#### Abstract.

In the present study we carried out nitroxide mediated radical polymerization (NMRP) of styrene in emulsion using 2,2,6,6-tetramethylpiperidine-N-oxyl (TEMPO) by stepwise and semibatch processes obtaining polystyrene (PS) with a polydispersity index (PDI) lower than 1.5 and particle diameter between 180 and 520 nm when methanol was used. Otherwise, when the polymerization was carried out in the absence of methanol, a bimodal particle size distribution (PSD) was obtained. This is attributed to the superswelling effect, which causes the particles to grow considerably and also to lower the nitroxide efficiency reducing chain formation and thus drastically reducing the particle nucleation. These polymerizations did not require a separate macroinitiator synthesis step, which represents an important advance for further applications.

#### 1. Introduction.

Free radical polymerization (FRP) is of enormous importance because approximately 50 % of all polymers are produced by this technique, which lately has undergo a revolution due to the advent of new techniques called controlled radical polymerization (CRP). One of the most important techniques of the CRP is NMRP which is a promising technique for obtaining tailor-made polymers in aqueous dispersed media which are of great interest for academic and industrial applications.[1] The success of this development depends very strongly of the understanding of scientific aspects which are still partially understood, such as colloidal stability at early stages of the process, the transport mechanism of reactants between the different phases and their interaction with the reaction mechanism. Therefore, the conception of simple and efficient conditions for successful aqueous dispersion processes represents an important challenge.[2] Early attempts to conduct stable TEMPO mediated emulsion polymerization of styrene resulted in severe coagulum formation.[1] Few works have been successful, notably Cunningham and coworkers who employed two nitroxides, TEMPO and 4-stearoyl TEMPO in ab initio emulsion polymerization of styrene obtaining an emulsion without coagulum, as well as excellent control/livingness. [3] Also, two step emulsion polymerization yields a coagulum free latex according to Georges and co-workers, who reported a successful seeded NMRP of styrene using a PS-TEMPO macroinitiator by use of a microprecipitation technique to generate the initial seed and subsequent swelling with styrene.[4] The use of a semibatch process is related with the reduction of particle superswelling, however few works using N-tert-butyl-N-(1-diethylphosphono-2,2dimethylpropyl)-N-oxyl (SG1) have been reported.[5, 6]

## 2. Experimental part.

## 2.1. NMRP in emulsion by a stepwise process.

In the first stage styrene, TEMPO and sodium dihexyl sulfosuccinate (MA-80) were mixed for 15 minutes, subsequently water (255 g) and potassium sulfate were added and mixed for 15 more minutes. The resulting mixture was charged into a 1.2 L Parr stainless steel reactor and purged with nitrogen for 30 minutes at room temperature and at an agitation speed of 300 rpm.

Subsequently the mixture was heated at 70 °C and a potassium persulfate solution (0.1996 g in 10 g of water) was added and the polymerization proceeded for 2 hours. Afterwards an MA-80 solution was added (6.5764 g in 20 g of water) and the temperature was increased to 135 °C for 1 hour and then the reactor was cooled at  $\approx$  35 °C. In the second stage styrene was added to swell the formed particles for 1 hour and then the temperature was increased at 135 °C and the reaction proceeded for 2 hours. Finally, the reactor was cooled at  $\approx$  35 °C and the third stage was started with the addition of styrene to swell the formed particles for 1 hour and then proceeded for 6.5 hours.

## 2.2. NMRP in emulsion by a semibatch process (RS-1).

This reaction was carried out under the same reaction conditions that in RL-1 (Table 1), only that at the end of the second stage at 135 °C the styrene feed was started (13 g) in a semibatch process with a flow rate of 0.0079334 g/min for 27.5 hours. The reaction mixture was heated for an additional 30 min after the styrene had been added.

## 2.3. NMRP in emulsion by a semibatch process using methanol (RS-2).

This reaction was carried out under the same reaction conditions that in RS-1 (Table 1) only that methanol was added in the first stage in order to minimize superswelling of particles.

In all previous cases the reactor was cooled to room temperature and samples were taken for their characterization, however, it was not possible to take samples along the reaction in order to determine the polymer chains grow and Dp.

Ex		Recipes of experiments									Operation conditions									
per	Styrene <sup>a</sup>		Water	Surfactan	t MA-80	MA-80 KPS	PS Potassium TEMPO M	Methanol	Temperature		e	Stirring	Monomor	Time						
ime	Stage 1	Stage 2	Stage 3	water	Stage 1	Stage 2	KI 5	Sulfate	TEMI O	wicutation	Stag	je 1	Stage 2	Stage 3	speed	addition	Stag	ge 1	Stage 2	Stage 3
nt	g	g	g	g	g	g	g	g	g	g	°C	°C	°C	°C	rpm	addition	h	h	h	h
RL-1	0.2	1.8	13	285	4.1467 <sup>b</sup>	6.5764 <sup>c</sup>	0.1996 <sup>d</sup>	0.3307 <sup>e</sup>	0.15 <sup>f</sup>	$0^{g}$	70	135	135	135	300	Stepwise	2	1	2	6.5
RS-1	0.2	1.8	13	285	4.1467 <sup>b</sup>	6.5764 <sup>c</sup>	0.1996 <sup>d</sup>	0.3307 <sup>e</sup>	0.15 <sup>f</sup>	$0^{\mathrm{g}}$	70	135	135	135	300	Semibatch <sup>h</sup>	2	1	2	27.5
RS-2	0.2	1.8	13	285	4.1467 <sup>b</sup>	6.5764 <sup>c</sup>	0.1996 <sup>d</sup>	0.3307 <sup>e</sup>	0.15 <sup>f</sup>	3.75 <sup>g</sup>	70	135	135	135	300	Semibatch <sup>h</sup>	2	1	2	27.5
<sup>a</sup> 5 % v	<sup>a</sup> 5 % weight.																			
ь 14.55	ig∕Lwa	ter = 1, 2	5 CMC (	(CMC	= 11.64 g/L	at 70 °C).														
° 23.07	g/L wa	ter.																		
<sup>d</sup> 0.70	03 g/L w	ater, TE	MPO/KI	PS = 1	.3.															
° 1.315	5 g/L wa	ter, equi	valent m	olar ra	tio to the in	itiator (2.5	g/L water	r).												
<sup>f</sup> TEM	f TEMPO/KPS = 1.3.																			
<sup>g</sup> 25 %	<sup>g</sup> 25 % weight ratio to the monomer.																			
h Flow	rate = 0	0.007934	g/min.																	

**Table 1.** Summary of emulsion polymerizations experiments.

## 3. Characterization.

Monomer conversion was determined gravimetrically. Gel permeation chromatography (GPC) was used to measure the molecular weight (MW) and the PDI of the polymer in a Hewlett Packard GPC Model 1100 equipped with a refractive index detector calibrated with standards of PS ranging from 580 to 3,900,000 g/mol. Tetrahydrofuran (THF) was used as the eluent with a flow rate of 1.0 mL/min. The Dp measurements were carried out by dynamic light scattering on a Zetasizer Nano S90 from Malvern Instruments at a temperature of 25 °C. Proton nuclear magnetic resonance (1H NMR) spectroscopy was performed on a FT-NMR Jeol Eclipse 300 MHz spectrometer at room temperature using CDCl3.

## 4. Results and Discussion.

## 4.1. NMRP in emulsion by a stepwise process.

The final conversion was 30.07 % (Table 2) with values of Mw = 31,453 g/mol, Mn = 24,863 g/mol and PDI =1.26 (Fig. 1), which indicate a good control of the polymerization. The nitroxide efficiency was 25.09 %, which indicates that the alkoxyamine formation in the first step was very low, which caused a reduced formation of Np = 4.71E+11, which is very low in relation to the values commonly obtained (1.0E+14). The low number of alkoxyamines formed and thus low Np is attributed to the extremely low solubility of TEMPO in water.[7] The value obtained for Dp was 426 nm, however, the PSD was bimodal (Fig. 1) showing a population centered in  $\approx 244$  nm and another in  $\approx 1,296$  nm.



Figure 1. Molecular weight distribution (left) and particle size distribution (right) of the polymerization RL-1.

However, once the latex was placed in the beaker (after  $\approx 30$  min) it started to destabilize showing a floating phase. This behavior is attributed to the presence of the high Dp population (1,296 nm), which may have caused the particle coagulation and therefore an unstable latex.[3-5] Another important factor that may have caused the phase separation is the particle superswelling because at the beginning of a NMRP a very high concentration of low MW oligomers are present at low conversion. This high concentration of oligomers and the absence of high MW polymer at low conversion can have a deleterious effect on the colloidal stability as a result of superswelling. If the superswelling is severe enough, formation of very large particles (>1  $\mu$ m) occurs, where buoyant forces dominate and a separate organic phase forms as an upper layer of the emulsion.[1, 8]

#### 4.2. NMRP in emulsion by a semibatch process (RS-1).

The strategy of this study was to avoid the monomer droplet formation through a slow rate of monomer addition in order to work under starved conditions and thus avoid superswelling. The final conversion was 34.84 % (Table 2) with values of Mw = 28,313 g/mol, Mn = 23,131 g/mol and PDI =1.22 (Fig. 2), which indicate the good control of the polymerization. The nitroxide efficiency was 24.79 %, which indicates that the alkoxyamine formation in the first step was also very low, which causes a low number of particles of Np = 3.63E+11. Similar to the last reaction (RL-1), the low number of alkoxyamine formed and thus low Np formed is attributed to the extremely low solubility of TEMPO in water. [7] The value obtained of Dp = 402 nm with a unimodal PSD (Fig. 2), represents a very good improvement compared to the last polymerization (RL-1). However, this PSD is still broad, varying in a range from 200 to 1,050 nm. Similary to the previous case, this behavior is due to the particle superswelling. [1, 8]



**Figure 2.** Molecular weight distribution (left) and particle size distribution (right) of the polymerization RS-1. However, in the same way as in the last case (RL-1), the latex started to destabilize after  $\approx 30$  min showing a floating phase. This behavior is attributed to the big particle size, which may have caused the particle coagulation and thus an unstable latex.

#### 4.3. NMRP in emulsion by a semibatch process using methanol (RS-2).

The strategy of this study was to minimize or avoid the superswelling effect through methanol addition because there are reports about the efficiency of methanol as particle deswelling agent.[9] The final conversion was 32.89 % (Table 2) with values of Mw = 31,395 g/mol, Mn = 22,501 g/mol and PDI =1.39 (Fig. 3). These results indicate good control of the polymerization. The nitroxide efficiency was 24.13 %, which indicates that the alkoxyamine formation was very low, which and ensuing low Np = 9.56E+11. Similar to the last reaction (RS-1), the low level of alkoxyamine formed and the low Np formed are attributed to the extremely low solubility of TEMPO in water. [7]The value obtained of Dp = 315 nm with a unimodal PSD (Fig. 3), represents a great improvement compared to the last polymerization (RS-1). The results were very good with respect to Dp and to the PSD because the values were between 180 and 520 nm, however, we still have low Np. This behavior is also due to the particle superswelling.



Figure 3. Molecular weight distribution (left) and particle size distribution (right) of the polymerization RS-2.

Again, the latex started to destabilize after  $\approx 30$  min. As suggested in previous cases the particle superswelling may have caused coagulation and thus unstable latex.

Figure 4 shows two pictures in which the obtained products before and after the destabilization can be seen.





**Table 1.** Summary of emulsion polymerizations results.

Ex	Results										
rper	Final	D	Coagulum	No	Molecu	lar weight		M theoretic	Nitroxide		
in	Conversion	Dp	Coaguium	мр	(g/	mol)	PDI	w <sub>n</sub> theoretic	efficiency		
ent	%	nm	g	Number	Mw	M <sub>n</sub>		g/mol	%		
RL-1	38.07	426	2.49	4.712E+11	31,453	24,863	1.26	6,239	25.09		
RS-1	34.84	402	2.86	3.6389E+11	28,313	23,131	1.22	5,735	24.79		
RS-2	32.89	315	2.95	9.568E+11	31,395	22,501	1.39	5,430	24.13		

1H NMR spectrum shows (Fig. 5) the presence of PS (7.25, 6.60, 1.86, 1.40 ppm) and the bond between PS and TEMPO assigned to the chemical shift between 3.8 and 4.2 ppm of the  $\alpha$ -hydrogen to the C-O bond. Also shown are the chemical shifts of the TEMPO end group between 0.4 and 1.15 ppm. The spectrum was similar for the three cases studied (chemical shifts). [10, 11]



Figure 5. 1H NMR spectrum of functionalized PS with TEMPO (RS-2).

## 5. Conclusions.

It was managed to significantly reduce the particle diameter (Dp) by using methanol, which it is believed to have decreased the particle superswelling. However, even when a narrow PSD was obtained, emulsion destabilization after reaction could not be avoided. Given the MW results, the low PDI and even in the face of low nitroxide efficiency, it can be concluded that the formation of dormant species in the first stage was achieved, followed by size increase in the next stages. The 1H NMR spectra reveals the presence of dormant species. The obtainment of stable latexes is a big challenge to overcome, however, the results obtained in the present study represent an important advance which opens a panorama of different strategies in order to minimize or avoid the emulsion destabilization. According to the strategy used, the partitioning coefficients of TEMPO between the organic an aqueous phase are very important data. These have recently been studied by E. Saldívar and co-workers, and it is expected that they could help to understand and solve the actual problem.

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## SYNTHESIS OF MESOPOROUS POLYSTYRENE NANOPARTICLES EMPLOYING SEMICONTINUOUS HETEROPHASE POLYMERIZATION

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Porous polymeric particles have been of increasing research interest-due to their promising applications in diverse fields such as chromatography, ion-exchange, cell immobilization, catalytic supports or drug storage and delivery; also porous polymeric particles with magnetic nanoparticles inside have been employed in chemotherapy [1-3]. Porous polymeric particles are usually synthesized by suspension or emulsion polymerization. Previous investigations [4] show that polystyrene mesoporous nanoparticles with narrow particle size distributions can be synthesized through the innovative semicontinuous heterophase polymerization employing divinylbencene as cross linking agent and toluene as porogen agent.

In the present communication we report the semi continuous heterophase polymerization of polystyrene mesoporous nanoparticles employing toluene as porogen agent and poly(ethylene glycol) dimethacrylate as the cross linking agent. Polymerizations were carried out at 60°C in a 150 mL glass reactor equipped with a reflux condenser and inlets of nitrogen, organic mixture feed, with a feed rate of 0.1 g/min, and sampling. We present the characterization of the material obtained, which includes conversion determined gravimetrically, particle size measured by transmission electron microscope (TEM), porosity and average pore radius determined in an automated surface area and pore size analyzer. Finally we discuss the influence of the polymeric cross linking agent in the pore size and the quantity of porogen agent needed in the polymerization reaction.

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#### METHYL METHACRYLATE-SURFMER COPOLYMER CONDUCTIVE NANOPARTICLES MADE BY HETEROGENEOUS-PHASE POLYMERISATION

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## Abstract

The synthesis of conductive nanosized particles were prepared in heterogeneous phase polymerization at 70 °C, using methyl methacrylate as monomer and a polymerizable lithium surfactant (surfmer) as stabilizer and co-monomer. The main purpose of employing this surfmer is to obtain conductive polymer nanoparticles for lithium batteries. The effect of polymer concentration on ionic conductivity on the latex were examined. Here, we obtained latex with polymer content higher than 8 wt. %, particles sizes in the nanometer range (< 100 nm) and conversions greater than 80 %. The ionic conductivity of the latex at room temperature is of the order of  $10^{-3}$  S/cm. In this polymerization process, the ionic conductivity increases as the polymer content is increased, i.e., a latex with polymer content of 5.5 wt. % has a conductivity of 2.4x10<sup>-3</sup> S/cm. The structure of the polymer was characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and differential scanning calorimetry (DSC).

## Introduction

In last years, lithium polymer battery has taken an important role in electronic devices, such as cell phone, automotive batteries, photo cameras. The first synthesis polymer electrolyte was performed in the 80s, obtaining a electrolyte polymer based poly(ethylene oxide) (PEO), formed by a complex between a lithium salt and a coordinating polymer[1]. In many reports, polymer properties are due to three components, polymer, lithium salt and solvent. Rajendran and Uma[2], prepared films from poly(methyl methacrylate) and LiBF<sub>4</sub> with different concentrations of plasticizer (dibutyl phthalate), where ionic conductivity of these polymer at room temperature was of the order of  $10^{-3}$  to  $10^{-4}$  S cm<sup>-1</sup> and increase proportionally to the temperature. Rubber natural grafted (MG30) with 30% poly(methyl methacrylate), which contained lithium salt (LiCF<sub>3</sub>SO<sub>3</sub>) and propylene carbonate or ethylene carbonate, has been studied and was reported that ionic conductivity increase with the amount doping agent[3]. Lee et al. [4], investigated a new class of lithium salt with single-ionic characteristics, lithium sulfonated styrene oligomer (LiSSO) [(CH<sub>2</sub>CHC<sub>6</sub>H<sub>5</sub>)<sub>7</sub>- $(CH_2CHC_6H_4SO_3Li^+)_2]$ , synthesized and prepared its complex with poly(ethylene oxide) (PEO). The maximum ionic conductivity of the PEO/LiSSO complex at 65°C was  $2.1 \times 10^{-4}$  S/cm at a salt concentration of  $[Li_+]/[EO] = 0.20$ . Other researchers have studied, the effect of plasticizer and TiO<sub>2</sub> nanoparticles on the conductivity, chemical interaction and surface morphology of polymer electrolyte of MG49-EC-LiClO<sub>4</sub>-TiO<sub>2</sub>. The highest conductivity of  $1.1 \times 10^{-3}$  Scm<sup>-1</sup> was obtained at 30 wt.% of EC[5]. The

objective of this work is to study the effect of polymer concentration on ionic conductivity of the latex, reaching a maximum polymer concentration of 8 wt.%.

## **Experimental part**

Polymerizations were carried out in a 250-mL jacketed glass reactor equipped with a reflux condenser and inlets for argon, monomer feed, sampling, and mechanical agitation. The reaction vessel was loaded with 0.37 g of surfmer, 33.6 g of water and different amounts of methyl methacrylate (2, 2.5 and 3 g), heated to 70 °C and bubbled with argon for 30 min before addition of AIBN (1 wt. % with respect to the monomer). The polymerization was performed in an hour. The conversion was determined by gravimetry and final latexes at the end polymerization were collected for particle size and ionic conductivity.

Average particle size (Dp<sub>z</sub>) was measured at 25°C by quasi-elastic light scattering (QLS) in a Malvern Zetasizer ZS90 apparatus. The particle size standard operating procedure subroutine was used to estimate the PSD. To eliminate multiple scattering and to measure the monomer-free average particle size, lattices were diluted with water up to 300 times. For measuring glass transition temperature, polymer was precipitated from the withdrawn samples by adding methanol (Bassel, reactive grade), then collocated in a membrane de Spectra/por <sup>®</sup>Dialysis Membrane (6000-8000 Dalton), to purify it. The ionic conductivity in latex was determined in an apparatus Xplorer GLX PS-2002, with conductivity sensor PS-2116A

#### **Results and discussion**

Figure 1 shows depicts QLS-measured z-average particle size  $(Dp_z)$  as a function of reaction time. Particle size is quasi-constant in course of the reaction, but its particle size is large, because the polymerization reaction only is carried out inside micelle, swelling.  $Dp_z$  increases systematically with increasing polymer content.



Figure 1. z-Average particle size (Dp<sub>z</sub>), measured by QLS versus polymerization time of MMA at different polymer content (5.5, 7 and 8 wt%).

Figure 2 it was observed that the ionic conductivity increased until  $2.63 \times 10^{-3}$  S/cm for 8 wt.%. PMMA-grafted natural rubber has been reported to exhibit ionic conductivity [6].

We suggest that conductivity of the latexes increase because more molecules of surfmer reactions with polymer chain, therefore, major amount lithium incorporated it.



Figure 2. Ionic Conductivity as a function versus Solid Content

A behavior characteristic of polymers that interact chemically with metals, complex salts, is an increase in the Tg as increases it [7]. In the figure 3, Tg slightly changes from 375.15 to 378.15 °K, viz., polymer content (5.5 and 8 wt. %), respectively. This increasing may be due to probable interaction between polymerizable lithium in main chains.



Figure 3. Glass transition temperature, Tg, of PMMA-surfmer for different polymer content: a) 5.5 and b) 8 wt %.

#### Conclusions

The latexes obtained shows a maximum ionic conductivity value of  $2.63 \times 10^{-3}$  S/cm. The amount polymerizable lithium surfactant is limited by solubility it, this keeps stability of nanoparticles, in this case study, stability maximum achieved was with a polymer concentration of 8 wt %. Finally, the increase in Tg indicates that

polymerizable surfactant interact chemically with poly(methyl metacrylate), this may explain the increases in the ionic conductivity with increase in concentration polymer.

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## PREPARATION OF DUAL STIMULI-RESPONSIVE NANOGELS BY ELECTRON BEAM IRRADIATION OF DILUTE AQUEOUS MICELLAR SOLUTIONS

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#### Abstract

Stimuli-responsive nanogels based on amphiphilic block copolymers crosslinked in the micellar state were prepared by means of electron beam irradiation. Block copolymers from PNIPAAm-*b*-PSt, PNIPAAm-*b*-PHA, poly(NIPAAm-co-5MPA)-*b*-PSt and poly(NIPAAm-co-5MPA)-*b*-PHA were used. The influence of the irradiation dose and the polymer concentrations were tested. The hydrodynamic radius ( $R_h$ ) was in the range of 30-50 nm, radius of gyration ( $R_g$ ) was within the range of 60-70 nm. The Nanogels showed a pH- and temperature-sensitive behavior in aqueous solutions that mimic biological conditions.

## Introduction

Nanosized hydrogels (nanogels) are polymer nanoparticles consisting of three-dimensional networks, formed by chemical and/or physical cross-linking of polymer chains. They have attracted growing interest owing to their potential for applications in drug delivery systems [1]. In the structure of nanogels, the presence of internal bonds gives fixed shape, higher resistance to degradation, and the ability to trap other molecules within their structure [2]. Due to the potential applications of nanogels several synthetic strategies were developed. Electron beam irradiation has already become one of the standard tools for the formation of nanogels. The procedure applied is usually based on the irradiation of dilute polymer solutions with a dose sufficient to obtain nanogels [2, 3].

## Experimental

## Materials

PNIPAAm-*b*-PSt (22,120 g/mol; 84:16 mol%), PNIPAAm-*b*-PHA (23,440 g/mol; 81:19 mol%), poly(NIPAAm-co-5MPA)-*b*-PSt (24,030 g/mol; 79:11:10 mol%) and poly(NIPAAm-co-5MPA)*b*-PHA (26,640 g/mol; 85:7:8 mol%) were used (Fig. 1). They were prepared by RAFT polymerization following a synthetic strategy described previously [4].



Figure 1. Amphiphilic block copolymers used.

#### **Electron Beam Irradiation**

Aggregates were prepared either via direct dispersion in water or in Buffer of pH 7.4; or by emulsion [5]. For that, a concentration of 1 mg/mL of amphiphilic block copolymer was used. Solutions were degassed by means of argon flux. The samples were irradiated by e-beam (Fig. 2) at a dose of 30, 60 or 120 kGy at room temperature in oxygen-free closed PE-bags. The electron beam irradiation was performed with an accelerator ELV-2 (Budker Institute of Nuclear Physics, Novosibirsk, Russia). The accelerator was operated with an energy of 1.0 MeV.



Figure 2. Aggregates crosslinked by e-beam.

#### **Light Scattering theory**

*Static light scattering (SLS)*. The angle dependence of the scattered light from dilute solutions has been analyzed in terms of the Zimm approximation assuming ideal behaviour (equation 1) [6].

$$\frac{Kc}{R_{\theta}} \approx \frac{1}{M_{\rm w}} \left( 1 + \frac{R_{\rm g}^2 q^2}{3} \right) \tag{1}$$

where *K* is an optical constant that is independent of the concentration of the solution and the molecular weight of the polymer, c is the concentration,  $R_{\theta}$  is the normalized scattering intensity (Rayleigh ratio) at the scattering angle  $\theta$ ,  $M_w$  is the weight-average of the molecular weight,  $R_g$  is the radius of gyration, and *q* is the magnitude of the scattering vector. The second virial coefficient  $A_2$  was calculated with the corresponding equation for hard spheres [7].

Dynamic light scattering (DLS). The decay time is related to the translational diffusion coefficient by

$$\Gamma = Dq^2 \tag{2}$$

where  $\Gamma$  is the exponential decay constant, *D* is the diffusion coefficient, and *q* is the scattering vector. The hydrodynamic radius (*R*<sub>h</sub>) is then determined from using the Stokes-Einstein relation for spheres

$$R_h = \frac{kT}{6\pi\eta_o D} \tag{3}$$

where k is the Boltzmann constant, T is the absolute temperature,  $\eta_0$  is the solvent viscosity and D is the diffusion coefficient determined from DLS data [7].

#### **Results and Discussion**

When dilute aqueous polymer solutions are subjected to ionizing radiation, polymer radicals are formed, which may decay by disproportion and recombination (crosslinking). Depending on the polymer concentration and on the dose rate two different crosslinking reactions can take place: inter and intramolecular crosslinking. If the irradiation dose and the distance between single polymer chains are high, the recombination of the formed radicals results mainly in an intramolecularly crosslinking [8].

In this work, amphiphilic block copolymers in the micellar state (small distance between single polymer chains) were irradiated by electron beam at dose relatively high (30, 60, or 120 kGy) to obtain core-shell nanogels. In this case, inter and intramolecular crosslinking may take place.

In the range from 0.2 to 1 mg/mL, the size of the nanogels did not showed a strong dependence on the blockcopolymer concentration used for irradiation. The SLS and DLS analysis of Net-[poly(NIPAAm-co-5MAP<sub>5%</sub>)-b-PHA] at different dose are shown in Fig. 3. In DLS, the linear relationship indicates that the samples have a single diffusivity and thus have a narrow size distribution (Fig. 3A). In SLS, the linear dependence on the scattering angle was also observed (Fig. 3B). The radius of gyration  $(R_g)$  and hydrodynamic radius  $(R_h)$  decrease slightly with increasing irradiation dose. The size of the nanogels decreases due to the increased crosslinking density. The values of  $A_2$  decrease with increasing radiation dose. The interactions within the polymer segments are getting more preferred to the interaction between the polymer segments and the solvent molecules (Fig. 4A). In Fig. 4B the sensitive behavior of these samples is observed. At pH 7.4, the nanogels showed thermal stability in the range of 24 to 46 °C. At, pH 5.8, the variation of size as a function of temperature decreases with increasing radiation dose, because of the increase in the rigidity of the structure. The sample irradiated at 30 kGy underwent more variation of size depending on the temperature ( $R_{\rm h}$ =41 nm at 24 °C;  $R_{\rm h}$ =35 nm at 38 °C;  $R_{\rm h}$ =33 nm at 46 °C) at pH 5.8. This sample exhibited a LCST of 18 °C at pH 4.0. The sample irradiated at 60 kGy showed linear dependence between size and temperature within the range of 24 to 42 °C at pH 5.8.



Figure 3. DLS (A) and SLS (B) of nanogels at different doses.



Figure 4. Effect of the irradiation dose on size (A) and thermosensitivity (B).

#### Conclusions

Sensitive nanogels from amphiphilic block copolymers were prepared by e-beam irradiation. The size of the nanogels decreased slightly with increasing irradiation dose. In the explored concentration range, the size of the nanogels did not showed a strong dependence on the blockcopolymer concentration used for irradiation. The *Net*-[poly(NIPAAm-co-5MAP<sub>5%</sub>)-*b*-PHA], irradiated at 30 kGy, showed a T/pH-sensitive behavior that mimic a drug carrier.

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## POLYMERIZATION OF VINYL ACETATE CATALYZED BY CYCLOMETALATED RU(II) COMPOUNDS

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VAc is one of the most challenging monomers for controlled/living radical polymerization because of its lacks of conjugating substituent, thus its propagating radical is highly reactive and tends to go by chain transfer and termination reactions. Recently VAc was polymerized with good level control via degenerative transfer approach using alkyl iodides [1] and Co-mediated process [2]. However, its polymerization via ATRP, one of the most versatile methods, has not been successful. The polymerization was not observed in the presence of Cu- and Ru-based catalysts. The polymerizations mediated by Fe-complexes resulted in the desirable product using  $CCl_4$  and alkyl iodide as initiator. But the polymerization initiated by  $CCl_4$  proceeded via telomerization mechanism based on redox initiation [3]. Polymerization with alkyl-I has better control, although the contribution of the iodine-transfer process cannot be fully excluded [4].

In this communication, we report the polymerization in solution of VAc with the cyclometalated Ru(II) complex [Ru( $\eta$ 6-C<sub>6</sub>H<sub>6</sub>)(dmba)(NCMe)]PF<sub>6</sub> as a catalyst in the presence of Al(Oi-Pr)<sub>3</sub> by conventional heating and microwave irradiation at 70 °C. The polymerization mediated by this catalyst, exhibit poor control with CCl<sub>4</sub> as initiator and obviously undergoes via telomerization mechanism. However this cyclometalated complex is successful in the Kharasch reaction with CCl<sub>3</sub>Br. Results using microwave irradiation as the heating source are similar to conventional heating; but decrease the reaction time.

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## SYNTHESIS OF AMPHIPHILIC SYMMETRICAL ABA TRIBLOCK COPOLYMERS PS-B -PEG-b-PS USING A BIFUNCTIONAL MACRO-RAFT AGENT

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#### Abstract

This study involves the synthesis and characterization of PEG-based amphiphilic block copolymers. PEG based difunctional macro RAFT agents were synthesized and characterized. PS-b-PEG-b-PS block copolymers were synthesized via the RAFT controlled free radical polymerization using the synthesized PEG dual macro RAFT agents. The content of polystyrene blocks on the triblocks was varied from 18% to 69% (based on molecular weight increase), adjusting the synthetic conditions.

#### Introduction

Block copolymers are a fascinating class of polymeric materials, since they offer the possibility to combine different properties along one macromolecular chain. The morphological features of block copolymers, especially tailor made diblock, triblock and higher block copolymers of different chain topologies has been an increasingly intense research subject during the last decades. Block copolymers, as a result of their tunable phase separation behavior, are key building blocks for a variety of functional nanostructured materials with potential applications ranging from electronic devices to drug delivery [1-4]. In particular, triblock copolymers have been identified as important components for the fabrication of highly functionalized nanomaterials.[5-8] Amphiphilic block copolymers consist at least of two incompatible polymer block chains that are

Amphiphilic block copolymers consist at least of two incompatible polymer block chains that are covalently connected, one polar block chain which is soluble in water (the hydrophilic group) and one nonpolar block which is insoluble (the hydrophobic group)[1-9].

## Experimental

## Synthesis of macro PEG difunctional RAFT agent.

The difunctional HO-PEG (10,000 g/mol), 4-(dimethyl amino) pyridine (DMAP) and RAFT agent 1 were dissolved in dichloromethane (DCM). 1,3-dicyclohexylcarbodiimide (DCC) was dissolved in DCM and slowly added to the reaction mixture. The reaction was allowed to continue for 1 week. Upon completion, the product was filtered off to eliminate urea and washed with water. The product was dried over magnesium sulphate, filtered off and the excess DCM was removed under reduced pressure. The product is a yellow solid.

#### Polymerization procedure in solution (Entry 4 in Table 1).

In a typical polymerization Macro PEG difunctional RAFT agent (1) (0.3 g, 0.028 mmol), Styrene (Sty) (0.278 g, 2.67 mmol), 4,4-azobis(4-cyanovaleric acid) (0.0028 g, 0.01 mmol), and 1,4-Dioxane/acetonitrile (4.0 mL) were mixed in a glass vial. This mixture was transferred to a 10 mL ampoule containing a magnetic stir bar. The oxygen was removed using 5 freeze-thaw evacuation cycles, and the ampoule was sealed with flame under vacuum. The solution was heated to 90  $^{\circ}$ C in an oil bath with magnetic stirring. At designated time, the polymerization was stopped by cooling

to room temperature. The polymerization yield was obtained gravimetrically by adding a fivefold excess of ethyl ether. The polymer product was purified by dissolution in the minimum amount of DCM followed by adding a fivefold excess of ethyl ether and decanting. This procedure was repeated three times to remove residual monomer followed by drying under vacuum to constant weight. Triblock polymer was obtained as a yellow solid, 17% yield (calculated by NMR).

#### Polymerization procedure in bulk (Entry 6 of Table 1).

In a typical polymerization Macro PEG difunctional RAFT agent (1) (0.3 g, 0.0277 mmol), Styrene (Sty) (0.55 g, 5.33 mmol), 4,4-azobis(4-cyanovaleric acid) (0.0017 g, 0.006 mmol) were mixed in a glass vial. This mixture was transferred to a 10 mL ampoule containing a magnetic stir bar. The oxygen was removed using 5 freeze-thaw evacuation cycles, and the ampoule was sealed with flame under vacuum. The solution was heated to 70 °C in an oil bath with magnetic stirring. At designated time, the polymerization was stopped by cooling to room temperature. The polymerization yield was obtained gravimetrically by adding a fivefold excess of ethyl ether. The polymer product was purified by dissolution in the minimum amount of DCM followed by adding a fivefold excess of ethyl ether and decanting. This procedure was repeated three times to remove residual monomer followed by drying under vacuum to constant weight. Triblock polymer was obtained as a yellow solid, 66% yield (calculated by NMR).

#### **Results and Discussion**

In this work we use a commercially available di-hydroxy-terminated PEG as starting material for the synthesis of a difunctional macro RAFT agent (hydrophilic segment, B). By transforming the hydroxyl group from PEG into the required macro RAFT agent on both ends of the PEG-chain. Finally we use the macro PEG difunctional RAFT agent to polymerize styrene blocks on both sides of PEG (hydrophobic segments, A) (Figure 1).

The focus of this investigation is the synthesis of copolymers with controlled structure in terms of the length of both the PEG block and the styrene block. With exact control of the hydrophobic:hydrophilic ratio (A, hydrophobic, B hydrophilic segments of the copolymer). The strategy was to use the following tri-thiocarbonate acid-functional RAFT agent (1) for the formation of the difunctional macro-RAFT agent for copolymer synthesis. A trithiocarbonate type of RAFT agent was selected to have a wider choice of monomers to block-copolymerize; it is known that trithiocarbonates works well for RAFT polymerization of styrenes, methacrylates, acrylates and acrylamides.





Triblock ABA Figure 1. Synthesis of difunctional macro- RAFT agent

As a result fo the block copolymerization with styrene, the PS segment of the polymer can be grown onto the macro RAFT agent at both ends of the PEG. A difunctional PEG macro RAFT agent, which will in turn lead to the formation of a ABA tri-block copolymer (Fig. 1). Table 1 shows result of copolymerization experiments in solution and in bulk. The obtained triblock copolymers show low polydispersities as determined by GPC. Furthermore, the molecular weights range from 13 thousand g/mol up to 35 thousand g/mol, all starting from a molecular weight of the macro-PEG of 10 thousand g/mol. This indicates that the ability to grow polystyrene is equal independently if we decide to grow short blocks or long blocks into de macro-PEG. Figure 2 shows FT-IR spectra for macro-PEG difunctional RAFT agent and triblock copolymer. Aromatic C-H stretching at 3010 cm<sup>-1</sup> is evidence of the presence of styrene in the triblock copolymer. Attempts to carry out synthesis of triblocks copolymers in solution at 70 °C resulted in bimodal molecular distributions, indicating that polystyrene was growing separately from the macro-PEG.

Table 1. Copolymerization of styrene using di-functional PEG macro RAFT agent at 90 °C (MW=10756 g/mol).

Entry	Concentration	Time (h)	Macro-PEG	Styrene	AZO	M <sub>n</sub> of Triblock	PDI
	(mM)"		(mmol)		(mmol)	by GPC (g/mol)	
1	4	23	0.028	5.33	0.010	13170	1.30
2	2	23	0.028	5.33	0.006	15330	1.11
3	2	23	0.028	5.33	0.010	17240	1.28
4	2	23	0.028	13.3	0.006	23290	1.31
5	4	40	0.028	5.33	0.010	14360	1.35
6 <sup>b</sup>		2	0.028	5.33	0.006	35410	1.23

<sup>a</sup>Mixture of *p*-dioxane-acetonitrile. <sup>b</sup>The polymerization was carried out at 70 °C in bulk.



Figure 2. FT-IR spectrum of a) Triblock PS-b-PEG-b-PS y b) macro-PEG difunctional RAFT agent

#### Conclusions

A difunctional macro-PEG RAFT agent based on trithiocarbonates was developed. Triblock copolymers were successfully prepared via RAFT copolymerization of styrene with the PEG-based difunctional macro RAFT agent prepared. The triblock copolymers were obtained by bulk polymerization and solution at 90 °C successfully. The styrene block copolymer content was varied at will from 18% to 69% conserving low polydispersities.

#### Acknowledgements

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## SYNTHESIS AND CHARACTERIZATION OF POLYACRYLAMIDE BY RAFT POLYMERIZATION

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#### Abstract

Currently, the use of macromolecules to include in the same structure two monomer units to provide different properties is increasing. The method of synthesis of these polymers can vary and can be difficult depending on the chemical nature of these monomers. An alternative synthesis process is the controlled-living polymerization techniques. In the present study was synthesized polyacrylamide by RAFT polymerization. The synthesis was carried out in solution polymerization. The agent used were benzyl ditiobenzoate (BDB).

The CTA and acetonitrile were added into a reactor equipped with condenser and mechanical stirrer. The mixture was vigorously agitated, purged with nitrogen during 1 h, and heated to 82 °C under agitation. Then, the initiator ACVA was added to the mixture to start the reaction, and bubbling was maintained during all the polymerization reaction, this step was run for 5 h. The polymer obtained was insoluble in acetonitrile. The polymer was recovered by filtration and washed with methanol to remove traces of residual monomer and initiator, and finally filtered and dried under vacuum at 40 °C for 48 h. The Mn was obtained by and <sup>1</sup>H NMR and SEC. The PDI was determined by SEC.

## Introduction

Water-soluble polymers represent an important class of macromolecules which have been utilized extensively in water treatment, mining, and enhanced oil recovery and as dispersants, stabilizers, coatings, etc., in personal care and pharmaceutical formulation.

Only recently, however, have techniques for precise synthetic design of architectures with specified molecular weights become available. These techniques, identified in the literature as controlled/"living" radical polymerization (CLRP) or simply controlled radical polymerization (CRP), have been the focus of extensive research as evidenced by the proliferation of manuscripts including several reviews. Of the CRP techniques, reversible addition-fragmentation chain transfer (RAFT) is arguably the method of choice for preparation of water-soluble (co)polymers. Not only can diverse classes of monomers with wide-ranging functionality be polymerized, but this can be accomplished directly in water, often without the necessity of protecting groups, provided judicious choice of chain transfer agents (CTAs), initiators, and reaction conditions.

In this paper we pretend to synthesize polyacrylamides by RAFT Polymerization. To do this we used the CTA benzyl dithiobenzoate (Figure 1). This initial investigation will be ground for the next synthesis of block copolymers and terpolymers.

## Experimental

## Synthesis of benzyl dithiobenzoate (BDB)

This compound was synthesized from phenylmagnesium bromide, carbon disulfide and benzyl. Phenylmagnesium bromide was obtained from the reaction of 0.3 moles of phenyl bromide with 0.31 moles of magnesium in dry THF and iodine as indicator. The beginning of the formation of PhMgBr occurred at 45 °C, at this temperature was observed a change in the color of the reaction mixture of red-brown to transparent. The reaction continued until the magnesium reacts completely, showing again a gradual change in color from clear to gray-green characteristic of the Grignard compounds. Then continued with the addition of 0.3 moles of carbon disulfide CS<sub>2</sub> diluted in 10 mL of dry THF in an interval of 30 minutes, the temperature was maintained at 45 °C. Finally the gradual addition of 0.31 mol of benzyl bromide, the reaction remained under stirring and inert atmosphere overnight. Purification of benzyl dithiobenzoate was performed by column chromatography using silica gel as packing and hexane as eluent. Yield 40.56%, the compound was characterized by <sup>1</sup>H and <sup>13</sup>C NMR and its structure was confirmed by GC/MS.

## Synthesis of polyacrylamide

The synthesis was carried out in solution polymerization. The CTA and acetonitrile were added into a reactor equipped with condenser and mechanical stirrer. The mixture was vigorously agitated, purged with nitrogen during 1 h, and heated to 82 °C under agitation. Then, the initiator ACVA was added to the mixture to start the reaction, and bubbling was maintained during all the polymerization reaction, this step was run for 5 h. The polymer obtained was insoluble in acetonitrile. The polymer was recovered by filtration and washed with methanol to remove traces of residual monomer and initiator, and finally filtered and dried under reduced pressure at 40°C for 48 h. The  $M_n$  was obtained by and <sup>1</sup>H NMR and SEC. The PDI was determined by SEC.



Figure 1. Benzyl dithiobenzoate

## **Results and Discussion**

In the first step the kinetic was performed by free radical polymerization of acrylamide. The results are shown in Table 1. The kinetics followed for 5 h, but from 60 min, conversion was above 90%. The polyacrylamide had a  $M_n$  of 150 000 g/mol and PDI of 2.

time h	Mn g/mol	PDI
1	102 600	2.16
2	106 900	2.158
3	110 500	2.139
4	138 900	2.065
5	157200	2.024

**Table 1.** Kinetics of polyacrilamide by free radical polymerization

Then we made a kinetic with a low concentration of CTA = 0.1 mM, under the same reaction conditions. According to the data obtained (Table 2), the PDI and  $M_n$  values were lower than in the case of the free radical polymerization, which is a proof of the living behavior in the reaction.

time h	Mn g/mol	PDI
1	104 500	1.957
2	97 390	1.888
3	86 940	1.818
4	81 040	1.725
5	69 210	1.719

Table 2. Kinetics of polyacrilamide with a CTA=0.1 mM

In order to obtain lower polydispersity values, the kinetics was performed at molar ratio of [CTA]/[I] = 1 and [CTA]/[I] = 2 mM. In this case the kinetics was followed by <sup>1</sup>H NMR. Figure 2 shows as disappear the signals corresponding to the monomer between 5.8 and 6.3 ppm at 5 h of reaction.



Figure 2. Kinetics of polyacrylamide followed by 1H NMR

According to the data obtained by SEC the polymer synthetized at 6 h had a PDI of 1.22 with a  $M_n$  of 3 000 g/mol.

## Conclusions

The transfer agent selected has a good control over the polymerization reaction of polyacrylamide even at low molar ratio of [CTA]/[I]. The living character offered by this RAFT agent is currently evaluated.

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## POLYSTYRENE "GRAFTING FROM" SILICA NANOPARTICLES FUNCTIONALIZED WITH NITROXIDE USING OXOAMMONIUM SALTS

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Several work groups have functionalized silica nanoparticles (NPSi) with nitroxide groups to obtain hybrids alkoxyamines, nevertheless, all these ingenious approaches involve several steps of synthesis and purification methods. Thus, the preparation of functional alkoxyamine is a complicated multistep process. On the other hand, there are a few explorations about synthesis of polymer/silica hybrid composites by nitroxide mediated polymerization in recent years[1].

In the present work we functionalize NPSi (A200, from Degussa) with TEMPO moieties (hybrid alkoxyamine) in a only one step of synthesis using oxoammonium salts (Br-TEMPO) at 2°C during 4h in the presence of tri-ethylamine and dichloromethane[2]. Using this proposed approach, we produce NPSi with different level of functionalization by varying the amount of salt added (S1F1, S1F3 and S1F5). The hybrid alkoxyamines were characterized by FT-IR and TGA analysis, in where high level of functionalization were founded.

In order to demonstrate the use of S1F1, S1F3 and S1F5 as hybrids alkoxyamines in the controlled graft polymerization of styrene (St) from their surface, was developed a kinetic of grafting in vials. Each vial was charged with St and functionalized silica and were placed into a recirculation heating bath at 125°C. After 30, 60 and 120 min. were recovered from the heating bath. The polymer formed containing NPSi was precipitate into methanol. The NPSi-g-PSt and "free" PSt were separated and the NPSi were dissolved to recover the PSt grafts. Grafts of polystyrene were characterized by GPC.

In all cases, grafts of PSt grow in controlled fashion: PD = 1.0 - 1.1 and a gradual shift of the chromatograms of GPC towards high molecular weights. In the case of S1F5, was less notorious this shift because containing more concentration of nitroxide.

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## FACILE EXPANSION AND FUNCTIONALIZATION OF GRAPHITE WITH NITROXIDE GROUPS

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### Abstract

Functionalization of carbon nanotubes (CN) with polymers have been widely studied however, CN functionalized with polymers are not available yet at industrial scale and are very expensive. On the other hand, Graphite Oxide (GO) under high both temperature and pressure leads to obtain Expanded Graphite (EG). GO is cheaper, available at large scale, and their expansion and functionalization, arises as a alternative to the CN.

In this work, a novel route to obtain EG and functionalized at the same time, using nitroxide groups is presented. Commercial natural graphite NG was expanded in the presence of solvent, nitroxides or initiator using one synthetic pathway. It is proposed that the defects in the surface of the platelets (double bonds) allow the abstraction of hydrogen atoms forming a radical centered in carbon which is trapped by the nitroxide, carrying out the functionalization of NG. EG and NG were characterized in detail by XRD and SEM. The results suggest that the NG was expanded around 20% by the covalent bonding of nitroxide groups to the platelets, which helps to the separation of graphite layers. The work proposed here has several advantages over the previous methods, including a high efficiency of expansion process, the use of a non-toxic intercalant, and the capability for mass production of expanded graphite for industrial applications.

#### Introduction

Currently, the use of graphite nanoplatelets (GNPs) has been of considerable attention as an alternative to metal and its low cost as conventional electrically conductive reinforcement, the composites with polymeric matrices GNPs are able to dissipate the load. [1] Some studies suggest that the composite undergoes a transition from insulator to conductor by gradually increasing the content of the conductive charging, and presents a typical behavior of percolation, which is attributed to the formation of several continuous paths for the electron or a transmission system in polymer composites with filler content above the percolation threshold. The problem of percolation of reinforced polymer nanocomposites GNPs is smaller than conventional loads, such as carbon fibers and carbon black, due to its extremely large surface area and their high aspect ratio of the GNPs. [1]

A number of works about growth and expansion of graphite have been reported. Among them, micromechanical cleavage is currently the most effective and reliable method to produce high-quality sheets of expanded graphite. However, the low productivity of this method makes it unsuitable for large-scale applications. [2]

In this first study, we speculate that using nitroxides, could be a advantage because these stable radicals can be react with the defects (double bonds) present in the graphite; these allows to find modest levels of expansion between the layers of the GN. This method involves only one chemical step under mild conditions, in which, surface is functionalized with organic groups (nitroxides). We speculated that the nitroxides can be of help to increase the degree of expansion, and the

surficial area due to the organic groups attached to each stack of graphite. This expansion, is necessary for increase the dispersion and compatibility of expanded graphite with the polymer matrix.

## Experimental

*Expansion using TEMPO and initiator:* The basic strategy involved in the expansion of natural graphite (GN) is carried out through the reaction with initiator and TEMPO to produce expanded graphite nanoplatelets (GNPs). The fabrication process is outlined in Figure 1. There are three main steps:

- (1) Natural Graphite was dispersed in a suitable solvent.
- (2) Graphite dispersion, TEMPO and initiator were stirred and heated in a small beaker.
- (3) On completion of the reaction, the mixture was filtered under vacuum, washed and finally dried under a vacuum.



Natural graphite

Figure 1. Process using TEMPO

*X-Ray Diffraction.* Analysis by X-ray diffraction was carried out on a PANalytical Empyream, radiation CuK $\alpha$ 1, Cu anode,  $\lambda = 1.54060$  A, operated at 35 mA, 40 kV, with a 2 $\theta$  scan of 9.9 at a 99.9 of total time in a continuous scan mode with a Bragg-Brentano geometry.

*Scanning Electronic Microscopy (SEM).* The surface morphology, was conducted by a 15kV HV SEM analysis in a SEM Field Emission Model FEI Nova 200 Brand NanoSEM. The sample preparation was performed using a drop of the dispersion on a sample holder for SEM. The study was performed using the secondary electron detector.

## **Results and discussion**



Figure 3. XRD patterns a) NG and b) GNPs

XRD patterns of samples from natural graphite and expanded graphite are showed in figure 2. In XRD pattern, the peaks coincide exactly, before and after treatment of expansion, the only difference, is the main peak intensity, which decreased from 49180 to 37380 counts. Using these values we calculate the percent of expansion, equivalent to reduction of 24%.

For NG peak intensity at  $2\theta = 26^{\circ}$  indicates a highly organized crystalline structure. The main peak for expanded graphite decreases its intensity. This was attibuted to: i) The graphite layers have been separated due to the presence of functional groups, and ii) the disordered structure of expanded graphite caused by the binding of functional groups.

det

Figure 3. SEM micrographs. a) NG and b) GNPs

SEM micrographs of NG and GNPs are presented in Figure 3a and 3b respectively. For NG stacks are observed with a flat and smooth, well-defined borders with a thickness of 100 nm, with dense distribution. For there is a distribution GNPs is less dense, irregularly shaped, rough surface, rounded edges and spots on the surface, probably due to the presence of organic groups have an increased separation and there are some platelets with thickness less than 100nm.

#### Conclusions

This study has provided a novel method in order to expand and functionalize natural graphite to produce GNPs, which can then be dispersed in polymer matrices or non-polar solvents.

This method is relatively inexpensive and friendly, because it involves a single step

The techniques used for characterizing reveals that the natural graphite was expanded slightly, in other words, TEMPO groups were intercalated into the galleries of the natural graphite.

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## AMPHIPHILIC BLOCK COPOLYMER FROM HYDROXYL-TERMINATED POLYMERS FUNCTIONALIZED WITH TEMPO. A NEW SYNTHETIC METHOD USING OXOAMMONIUM SALT<sup>†</sup>

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#### Abstract

This work presents a simple approach for the end-functionalization of hydroxyl-terminated polymers with nitroxide moieties using oxoammonium salts (OS). The functionalization is carried out using only one synthetic pathway in which are found high levels of functionalization (90%). A mechanism for the functionalization with TEMPO moieties using OS is proposed in which the formation of peroxide groups is suggested. The structures of the functionalized polymers are characterized in detail by <sup>1</sup>H NMR, <sup>13</sup>C NMR, DQF-COSY, and HETCOR. Bifunctional macroalkoxyamines are used to demonstrate how to extend the polymer chain for the synthesis of amphiphilic triblock copolymers by polymerizing St in a second block mediated by a nitroxide radical which provides the block length control.

#### Introduction

Great interest has been focused on functional polymers as building blocks for the synthesis of block and graft copolymers.<sup>[1]</sup> In particular, amphiphilic block copolymers are very attractive materials from both the scientific and the industrial point of view due to their hydrophobic/hydrophilic behavior.<sup>[2]</sup> In particular, the synthesis of triblock copolymers such as PSt-b-PPG-b-PSt, PSt-b-PDMS-b-PSt, or PSt-b-PEG-b-PSt using a prepolymer of poly(propyleneglycol) (PPG), polydimethylsiloxane (PDMS), or poly(ethylene glycol) (PEG), respectively, previously functionalized at the ends of each chain with nitroxide moieties, in the presence of styrene (St) monomer have been less studied. On the other hand, nitroxides are stable free radicals that in the presence of a specific counter-ion could lead to oxoammonium salts (OS).<sup>[3]</sup> This kind of salts are powerful, selective, and nonmetallic oxidants extensively used for the oxidation of primary and secondary alcohols to aldehydes and ketones, respectively.<sup>[4]</sup> But in the presence of a base (e.g., triethylamine, Et3N), its chemistry of oxidation radically changes to a chemistry of functionalization, which is not an obvious result. Nowadays, all strategies of synthesis developed to obtain amphiphilic diblock or triblock copolymers of PPG, PEG, or PDMS with PSt, using bifunctional macroalkoxyamines and St involve numerous synthetic pathways and sophisticated methods of purification. In this work we show a simple, direct, and general approach for the end-functionalization of hydroxyl-terminated polymers (PDMS, PEG, and PPG) with nitroxide moieties using OS [Br-2,2,6,6-tetramethylpiperidine-N-oxyl (TEMPO)] in the presence of Et3N in solution. Notice that, as far as we know, the OS has not been used before for this end in polymers.

#### **Experimental**

<sup>&</sup>lt;sup>+</sup> Macromol. Chem. Phys. 2011, 212, 1654–1662

*Synthesis of Oxoammonium Bromide Salt: Br-TEMPO*. Bromine was added to a solution of TEMPO. A brown solid (Br-TEMPO) was formed instantaneously and was purified by a Soxhlet extraction system using CCl<sub>4</sub>. Br-TEMPO salt was dried over vacuum at room temperature overnight.

*Synthesis of the Bifunctional Macroalkoxyamines.* Three kinds of macroalkoxyamines were synthesized. The reaction conditions for the functionalization of PPG (purified on a chromatographic column to remove the antioxidants), PEG, and PDMS with nitroxide moieties using OS are summarized in Table 1. Functionalize polymers were washed with THF, filtered and finally purified in a chromatographic column.

Table 1.	Reaction	conditions	for the	functionalization	of hydrox	xyl-terminated	polymers
with TEN	MPO moie	ties, using c	oxoamm	onium salt (OS, Bi	-TEMPO	).	

Polymer	Substrate	Am ount (g)	Mn (Da)	OH (mol)	OS (mol)	Et <sub>3</sub> N (mol)	CH <sub>2</sub> Cl <sub>2</sub> (mL)	Time (h)	Temp. (°C)
PPG-T	PPG	25	3500	0.041	$0.041^{a}$	0.045	100	12	60
PEG-T	PEG	1	600	0.004	$0.008^{b)}$	0.008	2.6	12	60
PDMS-T	PDMS	10	4250	0.005	$0.01^{b}$	0.02	10	24	40

<sup>a)</sup> Using a stoichiometric relation (1:1) of OH groups:OS and PPG purified (without antioxidant); <sup>b)</sup> Using an excess of OS (1:2) with respect to PEG or PDMS without purification.

*Synthesis of Amphiphilic Triblock Copolymers.* In order to demonstrate the extension of the polymer chain, we decided to use two bifunctional macroalkoxyamines for the synthesis of triblock copolymers of PSt-b-PPG-b-PSt and PSt-b-PDMS-b-PSt, respectively, by polymerizing St in a second block mediated by a nitroxide radical. Table 2 summarizes the reaction conditions for each case. The reaction mixture was purified in methanol twice, and the polymer obtained was characterized by SEM or TEM.

*Table 2.* Polymerization conditions used for the synthesis of amphiphilic triblock copolymers at 130  $^{\circ}$ C in toluene.

Copolymer	Bifunctional macroalcoxiamine		Amount (g)	Toluene (mL)	St		T (h)
	Туре	$\overline{M}_n(\mathbf{Da})$	-		( <b>g</b> )	(mL)	
PSt-b-PPG-b-PSt	PPG-T	4392	0.5	80	2.07	1.86	14
PSt-b-PDMS-b-PSt	PDMS-T	6170	5	20	15	13.5	4

#### **Results and Discussion**

*Proposed Reaction Mechanism.* The simple synthetic route, to obtain functionalized polymers at the ends of each chain with TEMPO moieties using OS (Br-TEMPO) is shown in Figure 1. The reaction mechanism proposed to obtain (2) involves a radical substitution by a free-radical process. In this reaction, it is assumed that the hydrogen atoms presents in the hydroxyl groups at the ends of each polymeric chain can be abstracted by a bromine radical generating hydrobromic acid (HBr). Thus, an oxygen-centered radical site at the ends of each chain is formed,<sup>[5]</sup> which is then quickly capped by the nitroxide radical in order to form (2). The HBr formed is trapped by Et<sub>3</sub>N to form triethylamine hydrobromide

(Et<sub>3</sub>NHBr). In a second stage, amphiphilic block copolymer (3) is formed using (2) in the presence of St and solvent at 130 °C during 14 h.



*Figure 1.* Schematic representation proposed of the functionalization of hydroxylterminated polymers with TEMPO using OS (Br-TEMPO) and their use in the synthesis of block copolymers.

*Functionalization of Hydroxyl-Terminated Polymers with TEMPO Using Oxoammonium Salts (Br-TEMPO): FTIR Analysis.* Unmodified PPG and PPG-T were characterized in detail. PPG: 3509, 1342, and 662 cm<sup>-1</sup> corresponding to stretch vibrations (O-H) of the intermolecular hydrogen bonding, CH-OH and out-of-plane OH bonding of the bend O-H group, respectively. In the region of 2867–2962 cm<sup>-1</sup> symmetrical ( $v_s$ ) and asymmetrical ( $v_{as}$ ) stretching vibrations of C-H, corresponding to CH<sub>2</sub> and CH<sub>3</sub> groups, were observed. A strong absorption band at 1094 cm<sup>-1</sup> was attributed to a stretching vibration from C-O-C. Also, a stretching vibration of C-O of primary alcohol was observed at 1012 cm<sup>-1</sup>. In case of PPG-T new bands at 3122 and 2759 cm<sup>-1</sup> was attributed to -CH2- and -CH3 groups of the piperidine ring from TEMPO. Also, at 724 and 614 cm<sup>-1</sup> were observed and were attributed to N-O bonds of the piperidine ring from TEMPO and NO-OC bonds (peroxide groups), respectively.<sup>[6]</sup> Notice that the broad vibration band at 3509 cm<sup>-1</sup> from PPG is not present in the PPG-T spectra which, jointly with the vibration at 614 cm<sup>-1</sup>, suggests that the functionalization was successful.

*NMR Analysis.* The structure of the unmodified and functionalized polymers was evidenced by NMR. In the case of PEG unmodified, the polymer only exhibit typical resonances centered at  $\delta$ =3.2ppm attributable to hydroxyl groups from the alcohol –CH<sub>2</sub>-OH of the hydroxyl terminated PEG. At  $\delta$ =3.53ppm was observed a resonance attributed to two protons of the –OCH<sub>2</sub>– group.<sup>[7]</sup>. PPG showed typical resonances centered at  $\delta$ =1.1, 3.4 and 3.63 attributed to –CH<sub>2</sub>–, –CH–, and –CH<sub>3</sub> groups, respectively. In the PEG-T structure, new resonances were observed centered at  $\delta$ =1.36, 1.63, 1.81, and 2.15ppm attributed to – CH<sub>2</sub>– groups of the piperidine ring from TEMPO and resonances centered at  $\delta$ =0.3 and 0.2ppm were attributed to –CH<sub>3</sub>– groups from TEMPO. In the case of PPG functionalizated with TEMPO was observed the same resonances that in the case PEG-T. All these new assignments were confirmed by <sup>13</sup>C NMR, DQF-COSY, and HETCOR.

*Functionalization efficiency.* Based in the experimental chemical shifts, the new chemical composition was estimated and the degree of functionalization. The chemical shift in the range of  $\delta$ =1.83–2.15 (-CH<sub>2</sub>-) was considered for the estimation of the final chemical

composition in all cases (PPG-T and PEG-T). The efficiencies of functionalization obtained by <sup>1</sup>H NMR and by titration with iodine (as indirect test) are shown in Table 3. In Table 3, we can observe that the key to obtain high values of functionalization (f) is to remove the antioxidants present in the prepolymer prior to functionalization. The degree of functionalization was calculated according to the Equation 1

Ec. 1 degree of functionalization =  $\frac{\text{amount of nitroxide from }^{1}\text{H NMR}}{\text{amount of OH capable of functionalization}} \times 100$ 

Polymer	Amount of OH available for functionalization (mol)	Nitroxide content (by <sup>1</sup> H NMR) (mol)	Degree of functionalization (%)		
			<sup>1</sup> H NMR	Titration	
PPG-T	0.041	0.0369	90	88	
PEG-T	0.004	0.0036	90	89	
PDMS-T	0.005	0.0024	50	45	

*GPC Analysis.* In order to demonstrate the application of the previously functionalized polymers (PPG-T, PEG-T, and PDMS-T) as bifunctional macroalkoxyamines in the controlled chain extension polymerizing St monomer as second block and confirm the possibility of synthesizing block copolymers, we decided to study for the PPG-T and PDMS-T, the chain extension by GPC to obtain block copolymers of PSt-b-PPG-b-PSt and PSt-b-PDMS-b-PSt. Thus, Table 4 shows the gradual shift of the molecular weights towards high molecular weights exhibiting low polidispersities, indicating that the chains of polymer were growing in a controlled fashion.

*Table 4*. The GPC analysis shows the increment of molecular weights to higher and narrow polidispersities.

	PPG- OH	PPG-T	PSt-b- PPG- <i>b</i> -PSt	PDMS- OH	PDMS-T	PSt-b-PDMS-b- PSt
$\overline{M}_n(\mathbf{Da})$	3500	4392	5967	4250	6170	7374
PD	1.03	1.1	1.37	1.5	1.6	1.64

*Morphology.* In the figure 2A is observed a microphase segregation (as in HIPS case) reveling spherical morphologies. The sample was not stained, thus the continuous phase is attributed to PSt domains. In the figure is observed that spheres formed presents similar sizes, this because the control that the nitroxide provides. In the figure 2B, the same sample was annealed with toluene vapors by 10 min at room temperature the spherical, domains showed a rearrangement, exhibiting a more ordered packing and, as a consequence, a smaller distance between them.



*Figure 2.* SEM images. A) PSt-b-PPG-b-PSt and SEM analysis obtained by casting (THF). B) PSt-b-PPG-b-PSt and SEM analysis (after annealing with toluene).

#### Conclusions

Hydroxyl-terminated polymers can be functionalizated using oxoamonium salts (Br-TEMPO) giving as result a bifunctional macroalcoxiamine which was experimentally corroborated by FT-IR, <sup>1</sup>H NMR, and <sup>13</sup>C NMR. This macroalcoxiamine was employed in presence of styrene monomer to the synthesis of aphiphilic block copolymers. The oxoamonium salts are strong candidates to the functionalize polymers with OH groups situated at the end of the polymeric chain. Was proposed a new mechanism of functionalization in where peroxide groups are formed. Also was demonstrated that bifunctional macroalcoxiamine in presence of styrene monomer can produce block copolymers, this was demonstrated by GPC in where obtain narrow polidispersities and higher molecular weights. Finally, the morphology of the block copolymer was evidenced as spherical morphologies.

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## CONTROLLED RADICAL POLYMERIZATION OF METHYLBENZYL METHACRYLATE

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#### Abstract

A comparative study of the reversible addition–fragmentation chain transfer and free radical polymerizations of  $\alpha$ -methylbenzyl methacrylate ( $\alpha$ -MBM) in solution at 70 °C using 1-phenylehtyldithiobenzoate (1-PEDB) as RAFT agent and AIBN as thermal initiator is showed. Polymerization rates in RAFT polymerizations are lower than in conventional free radical polymerization. Conversion *vs* time profile indicated that the polymerizations followed first order kinetics. By NMR and UV-Vis confirmed the presence of thiocarbonylthio moieties (SCS) in the polymer chains. The molecular weight distributions (MWDs) were moderately narrow (D 1.59 - 1.12)

#### Introduction

The main advantages of free-radical chemistry are the undemanding conditions required for polymerization and the large number of monomers that can be polymerized. The disadvantage of this method lies in the uncontrollable polymer structure. However, the application of living free-radical polymerization has opened the possibility of generating controllable macromolecular architectures with mild reaction conditions. The RAFT technique is probably the most versatile because it exhibits a high degree of compatibility with a wide range of functional monomers and is tolerant of water and oxygen in the system [1]. RAFT process is a polymerization in the presence of a dithio derivative that reacts by a series of reversible addition–fragmentation steps (Scheme 1).

$$P_{n} + \sum_{Z}^{C} - S - R \xrightarrow{k_{add}} P_{n} - S - C - S - R \xrightarrow{k_{\beta}} P_{n} - S - C - S - R \xrightarrow$$

Scheme 1. Fundamental reaction step in the RAFT mechanism proposed

Our group is focused on the CRP kinetics studies of functional monomers [2], in this sense it was previously evaluated the ATRP and RAFT polymerization of N-(S)- $\alpha$ -methylbenzyl methacryloylamine (N-(S)- $\alpha$ -MBMA) [3, 4] and also the ATRP of the  $\alpha$ -methylbenzyl methacrylate ( $\alpha$ -MBM) under different reaction conditions [3]. Now, in the present contribution the RAFT polymerization of  $\alpha$ -MBM is evaluated.

#### **Experimental**

#### Synthesis

The monomer  $\alpha$ -methylbenzyl methacrylate ( $\alpha$ -MBM) was synthesized according to follow procedure: methylbenzyl alcohol (0.206 mol) without solvent was reacted with freshly distilled methacryloyl chloride (0.309 mol) and 33.4 mL of a 37% NaOH solution. After 6 h, the mixture was filtered to separate the two liquid phases from the salt formed, the oily phase was treated several times with a 10% Na<sub>2</sub>CO<sub>3</sub> solution to obtain an uncolored liquid with a yield of 68%. IR (KBr), v(cm<sup>-1</sup>): 1717 (s, ester, vC=O), 1156 (s, ester, vC-O), 1635 (s, vinyl, vC=C), 942(s, \deltaCH,

CH2=). 1H NMR (CD3Cl, 300 MHz)  $\delta$ : 1.6 (d, 3H, CH3), 2.0 (s, 3H, CH3), 6.0 (t, 1H, CH), 6.2 (s,1H, CH2=), 5.6 (s, 1H, CH2=), 7.4-7.2 (m, 5H, Ar). 1-Phenylethyl dithiobenzoate (1-PEDB) was synthesized as reported by Le et al. [5]. <sup>1</sup>H NMR,  $\delta$  (ppm): 1.8 (d, 3H, CH<sub>3</sub>CH), 5.3 (q, 1H, SCHCH<sub>3</sub>), 7.2-8.0 (m, 10H, ArH). <sup>13</sup>C NMR,  $\delta$  (ppm): 20 (CH<sub>3</sub>), 50 (SCH), 126-146 (ArC), 227 (C=S).



Scheme 2. Structures of the RAFT agent and monomer

#### Characterization

NMR spectra were obtained on a Varian Mercury VX300-MHz, UV-vis spectra were obtained in chloroform at 25 °C using a quartz cell of 1 cm with an Ocean Optics SD2000 spectrometer. Molecular weight data (Mw) were determined on a multi-angle light scattering detector (DAWN Heleos from Wyatt) and molecular weight distributions were measured by size exclusion chromatography (SEC) on a Hewlett Packard modular system with a mixed PL Gel columns (1 K– 4 M) using a differential refractive index detector (HP 147 A). The eluent was THF (HPLC grade) at flow rate of 1 mL/min at 40 °C. The system was calibrated using narrow polystyrene standards (ranging from 162 to  $6.8 \times 10^6$  g/mol).

#### Dilatometry

The polymerization reactions were monitored through a well-established dilatometric method. Monomer conversion was traced using a contraction factor k, according to  $x = \Delta V/Vk$ . Here  $\Delta V$  is the change in volume present in the capillary; V is the initial solution volume.  $\Delta V$  is determined by  $\pi r 2\Delta h$ ; where r is the inner capillary radius and  $\Delta h$  is the change in height of the solution contained in the capillary (both expressed in cm), k was experimentally calculated from  $(\rho_p - \rho_m)/\rho_p$  ratio, where  $\rho_p$  and  $\rho_m$  are the densities of the polymer and monomer, respectively. The density values were measured by a pycnometric method.

#### **Results and Discussion**

The conversion profile decreases significantly when the 1-PEDB is added into the reaction with respect to the blank experiment (see Figure 1a and 1b). In addition, Figure 1c shows that the kinetics adequately fit a first-order reaction (like show the R-square values), which indicated that the propagating radical concentration remained nearly constant throughout the reaction as is expected for the living systems.


**Figure 1** Kinetics polymerization of  $\alpha$ -MBM at [M] $_0=0.2$  ( $\blacklozenge$ ), 0.5 ( $\bullet$ ), 0.7 ( $\blacktriangle$ ) and 1.0 M ( $\blacksquare$ ). [I] = 2 x 10-3 M at 70 °C, in toluene a) conventional free polymerization and RAFT polymerization b) conversion profile and c)  $\ln[M]/[M]_0$  trend

<sup>1</sup>H NMR spectrum of the poly( $\alpha$ -MBM) using 1-PEDB as RAFT agent displayed a weak signal at around of 7.5 ppm, which is assignable to aromatic protons from of the RAFT fragment (see Figure 2a) [6]. To confirm the presence of the -SC(S)- groups incorporated into polymers, the UV-vis spectra of polymers synthesized with and without RAFT agent were recorded (Figure 2b).



**Figure 2** a) <sup>1</sup>H NMR spectrum in CDCl3 of poly( $\alpha$ -MBM) synthesized in presence of 1-PEDB and b) UV-vis spectra comparison of poly( $\alpha$ -MBM) synthesized with and without RAFT agent and the UV-vis spectrum of 1-PEDB.

Molecular weight ( $M_w$ ) data of polymers synthesized by free radical polymerization are summarized in Table 1, and  $M_w$ ,  $M_n$  and polydispersity of 1-PEDB mediated polymerizations of  $\alpha$ -MBM are shown in the Figure 3, as it can seem the molecular weight distributions (MWDs)

were moderately narrow (D 1.59 - 1.12) and are lesser than corresponding in conventional polymerization.

**Table 1.** Molecular weight data obtained by MALS for the free radical polymerization of  $\alpha$ -MBM at fixed [I]<sub>0</sub> = 2 10<sup>-3</sup> M.

[M] <sub>0</sub>	% conversion	M <sub>w</sub> (g/mol)
0.2	3.85	39 310
0.5	8.65	103 300
0.7	12.5	252 600
1.0	15.86	714 900



Figure 3. Evolution of the molecular weight distribution for 1-PEDB mediated α-MBM polymerization

#### Conclusions

Kinetics of the free radical and RAFT polymerizations of  $\alpha$ -MBM was successfully monitored by dilatometry. Conversion *vs* time profile indicated that the polymerizations followed first order kinetics. <sup>1</sup>H NMR and UV-Vis studies confirmed the presence of thiocarbonylthio moieties (SCS) into the polymer chains. Polydispersity index (D 1.1 - 1.59) indicated that the control of the reaction is moderately good using 1-PEDB, which is a typical RAFT agent.

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## SYNTHESIS AND CHARACTERIZATION OF DI-, TRI- AND MULTI-BLOCK COPOLYMERS BASED ON POLY(E-CAPROLACTONE) AND POLY(LACTIC ACID)

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The aim of this work was to synthesize and to characterize di-block, tri- and multi-block copolymers based on aliphatic polyesters such as polylactic acid (PLA) and poly(e-caprolactone) (PCL). These materials have been chosen due to their biodegradability as well as biocompatibility properties. Moreover PLA and PCL are promising materials in regenerative medicine, they present good processability, mechanical properties and shape memory effects[1-2].

The specific goal of this research was to study the effects of the molecular weight on the crystallinity and on the morphological architectures of PCL-b-PLA di-block, PLA-b-PCL-b-PLA as well as PCL-b-PLA-b-PCL tri-block and multi-block copolymers[3].

Different PCL-b-PLA and PLA-b-PCL for the di-block as well as PCL-b-PLA-b-PCL and PLA-b-PCL-b-PLA for the tri-blocks have been synthesized by Ring Opening Polymerization, varying both the length of the blocks and the relative content of each block in the copolymers

The morphology-property relationships have been analyzed by nuclear magnetic resonance spectroscopy (NMR) allowing the assignment of the block-length and the molecular weight of each synthesized di- tri- and multi-block copolymers.

The influences of the nature of the block copolymers and the amount of each block in the amorphous and/or crystalline nature of the di-block as well as of the tri-blocks have been verified by DSC thermograms and by Small Angle X-Ray Scattering (SAXS) experiments.

The crystalline nature of PLLA is not influenced by the presence of PCL. For MnPLLA > 980 g/mol the PLLA is crystalline. The crystalline nature of PCL is influenced by the presence/nature of PLLA.

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## SYNTHESIS OF A NOVEL POLYASPARTATE MACROINITIATOR AND ITS COPOLYMERIZATION WITH STYRENE

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In recent years, the development of green chemistry has play a main role in the discovery and progress of new synthetic routes of chemical processes, always using renewable feedstocks, optimized reaction conditions and better catalysts for improvement of selectivity and energy minimization, as well as regarding the design of bio-/environmentally compatible compounds and materials [1].

The importance of polymeric materials incorporating biodegradability and biocompatibility is increasingly been recognized for a large number and variety of applications. Thus, the macromolecular design and synthesis of these polymer has been extensively studied in recent years. Among these polymers, poly (amino acids), having a protein-like amide linkage, are known as biodegradable polymers, and has been used for medical, cosmetic, and other industrial materials. Specially, poly(aspartic acid) (PASP) is a promising water-soluble and biodegradable polyamide that can be obtained from the hydrolysis of polysuccinimide [2].

In this work, we describe the functionalization of PASP with cyanovaleric acid in order to use it as a macroinitiator for its copolymerization with styrene. In a first step, the polysuccinimide (PSI) was obtained by polycondensation of aspartic acid. Then, the PSI was hydrolyzed and functionalized with cyanovaleric acid. The synthesized macroinitiator was used to initiate a free-radical polymerization of styrene. The copolymer thus obtained shows the structural advantages of the polystyrene combined with the biodegradable properties and hydrophilic character of PASP.

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## INFLUENCE OF HYDROPHOBE, SURFACTANT AND SALT CONCENTRATIONS IN HYDROPHOBICALLY MODIFIED ALKALI-SOLUBLE POLYMERS OBTAINED BY SOLUTION POLYMERIZATION

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#### Abstract

The rheological properties of hydrophobically modified alkali-soluble polymers to different hydrophobic macromonomer concentrations in the presence of various concentrations of anionic surfactant and salt were investigated. Associative polymers containing both ionic sites and small number of hydrophobic groups were prepared, and their thickening properties in aqueous solution were investigated. Solution polymerization was used for obtained the different polymers. Relationships between hydrophobe, sodium dodecyl sulfate (SDS) and salt (NaCl) concentration are proposed. Owing to the competition between attractive hydrophobic interaction and repulsive electrostatic interactions, such hydrophobically modified polymers exhibit various rheological behavior in aqueous solution depending on hydrophobic macromonomer, SDS and NaCl concentrations.

#### Introduction

Water-soluble polymers modified with relative low amount of a hydrophobic comonomer (< 5 mol%) have been the subject of extensive research efforts during the past decade because of their interesting rheological behavior in aqueous solution[1-16]. Intermolecular associations give rise to enhanced viscosification properties.

On the other hand, polyelectrolytes have been known for a very long time as efficient thickeners, specially in salt-free solution, because of intermolecular charge-charge repulsions that lead to coil expansion.

For the production of thickeners with improved properties, we therefore considered water-soluble polymers containing both hydrophobic and ionic groups in order to combine the advantages of polymolecular association and the polyelectrolyte effect [17-22].

To enhance the performances of associative polymers in paint and coating application, a better understanding of the associative interactions between associative polymers and salt and surfactant is needed. Depending on the nature of the additives, the thickening behavior can either decrease or increase. Over the last 30 years, most of the studies focused on the behavior of hydrophobically modified ethylene oxide urethane (HEUR) thickeners.[1-6] Some studies on hydrophobically modified alkali-soluble emulsion (HASE) polymers have recently been reported.[7-12]

HASE polymer can be classified as a hydrophobically modified polyelectrolyte. When neutralized in aqueous solution with suitable base, the latex particles are ionized as a result of the acid-base reaction. The partially neutralized polymer becomes water soluble and the polymer chains expand

owing to the mutual repulsion of the negative charges along the polymer backbone. Beyond a certain polymer concentration, the hydrophobic moieties along the polymer backbones associate inter-molecularly to form a network structure. This network structure greatly increases the solution viscosity and thickens the solution significantly. Addition of small salt concentrations removes the electrostatic repulsion between charges on the polymer backbone, which decreases the stiffness of the polymer chain. The conformation changes of the polymer chain from one of high to lower persistent chain length disrupt the intermolecular junctions. This causes the polymer network to collapse, reducing the hydrodynamic volume occupied by polymer chains and micellar clusters, thereby lowering the viscosity. By introducing sufficient amounts of surfactant, the active junctions can be strengthened by the adsorption of surfactant molecules decreases the functionality of polymer junctions. Consequently, a larger number of mechanically active junctions are assembled, which give rise to enhanced rheological properties.

We report here some results of an investigation into the synthesis, characterization, and solution properties of different polymers containing methacrylic acid, ethyl acrylate and an hydrophobic macromonomer obtained by solution polymerization. The specific features of the copolymerization methods used as well as their influence on the copolymer microstructure were examined. The aqueous solution properties of the copolymers were studied in the steady-shear viscosity properties in the absence and the presence of surfactant and salt. We compared the thickening abilities of the various samples, giving special attention to the effect of hydrophobic macromonomer, surfactant and salt concentration.

### Experimental

#### **Polymer synthesis**

Terpolymers of methacrylic acid (MAA), ethyl acrylate (EA) and a macromonomer (MM) were prepared by solution copolymerization method. Three different polymers were prepared. Typical experimental condition were as follows: In a flask ball three neck, equipped with condenser, magnetic stirring and oil bath temperature-controlled, were added the ethyl acrylate (EA), methacrylic acid (MAA), macromonomer (MM), ethyl alcohol (EtOH) and 1 wt% of AIBN with respect to total feed monomers, immediately the flask was keep in the oil bath at 70 °C. Polymerization was carried out for 2 h under an argon atmosphere. A polymer without MM was synthesized using the same reaction conditions to compare the rheological properties. After the polymer was precipitated and purified using hexane. The polymer was dried under vacuum at 50°C. The total solid concentration in the polymerization was keeping constant to 63.1 wt% in the systems. The characteristics of the polymers are given in Table 1.

Molecular Weight. The molecular weights of the samples were determined by size exclusion chromatography (SEC) (using THF grade HPLC as solvent), on a HPLC Hewlett Packard serie 1100.

Characterization. The composition of polymers was determined by 1H-NMR spectroscopy using 1 wt% solution in CDCl3 at room temperature in a JEOL 300 MHz spectrometer.

Polymer	Composition (g)/(mol)	EtOH	Conversion	SEC	SEC	Ip
	MAA/EA/MM	(g)		Mn	Mw	Mn/Mw
B0	16.6/16.6/0					
	0.1658/0.1928/0					
B1	16.6/16.6/4.1	22.0	99	78477	159485	2.03
	0.1658/0.1928/0.00546					
B2	16.6/16.6/10.8	26.0	94	71659	140404	1.96
	0.1658/0.1928/0.01708					
B3	16.6/16.6/16.6	29.3	91	69758	127046	1.82
	0.1658/0.1928/0.02614					

Sample preparation. Solutions of polymer were prepared by directly dissolving of 1.5 wt% of polymer into deionized distilled water, all of the polymer solutions were neutralized to a pH  $\sim$  9 with small amounts of concentrated 2-amino-2-methyl-1-propanol (AMP) solution, the correct amounts of SDS (5, 10 and 15 mM) and NaCl (0.05, 0.1, 0.2, 0.3, 0.4 and 0.5 M) were added to the system and each solution was gently stirred until the solution were homogeneous.

Rheological measurements. Rheology determinations were performed at 25°C in a Paar Physical UDS 200 controlled stress rheometer using either a cone and plate geometry (2° angle and 50 mm diameter). The zero shear viscosity was obtained by extrapolation of the apparent viscosity at very low shear rate.

#### **Results and Discussion**

Figure 1 shows the apparent viscosity ( $\eta$ ) as a function of the shear rate ( $\gamma$ ) for the four samples studied. The B0 sample shown a Newtonian behavior to all the shear rate studied. The samples containing hydrophobic groups (B1,B2 and B3) shown the same behavior but different viscosity, to small shear-rate, the systems are Newtonian; that is , there is no detectable variation of  $\eta$  with  $\gamma$ , when the rate is augmented, the Newtonian behavior is followed by a shear-thinning behavior; this shear-thinning is due to the breakdown of the intermolecular hydrophobic interaction, which produce a decrease in viscosity. We observed that the viscosity is increase when the sample have more hydrophobic macromonomer, that is, B0 < B1 < B2 < B3.



Figure 1. Variation of the apparent viscosity ( $\eta$ ) versus shear-rate ( $\gamma$ ) of the four samples synthesized. C = 1.5 wt%.

Figure 2 shows the variation of the steady-state viscosity  $\eta$  as a function of shear rate  $\gamma$  for B3 sample at different SDS concentrations, in aqueous solution. The sample without SDS present a large Newtonian behavior follow for a small shear thinning behavior, and low viscosity (~ 100 mPa.s); when SDS is aggregate, the viscosity increases drastically, and the samples exhibit a stronger shear thinning behavior. The maximum viscosity observed as a function of SDS was at 10 mM concentration, followed by a decrease of viscosity at 15 mM of SDS.



Figure 2. Variation of  $\eta$  as a function of  $\gamma$  for the B3 polymer at different SDS concentrations. C = 1.5 wt%.

Figure 3 shows the  $\eta 0$  as a function of SDS concentration (CSDS) for the three polymers studied. It is observed that the addition of surfactants to the solutions of associative polymers has dramatic effects on the rheological properties of the medium because links represent associative polymer micellar high-affinity domain interactions with surfactants [23-30]. In many cases, has been found that this effect is strongly dependent on the nature and level of addition of surfactant. The classical behavior of this mixture associative polymer/surfactant is: there is an increase in viscosity when SDS is added, reaching a maximum in this case the three samples presents this maximum to CSDS = 10 mM, to concentrations SDS higher (> 10 mM) show a decrease in viscosity. This behavior is attributed to the fact that the added surfactant molecules allow the formation of more hydrophobic domains and the formation of surfactant-polymer micelles. As a result, the average distance between micelles decreases. This allows the conversion of bound chains interlinked networks and strengthening networks with corresponding changes in viscosity, reaching an optimal concentration of surfactant. The observed decrease in viscosity above this surfactant concentration is attributed to an increase in the number of surfactant micelles lose their chance meeting with a hydrophobic group of a different polymer chain in a given micelle, and thus the network hydrophobic groups dispersed and solubilized by the surfactant. The B0 behavior is already reported for the system without hydrophobic groups, a Newtonian comportment as a function of the surfactant concentration is observed at all the surfactant concentrations studied, the surfactant quantity added not modified the viscosity of the samples due the absence of hydrophobic groups. The different viscosity presented by the samples (B3 > B2 > B1 > B0) is due to hydrophobic concentration in the terpolymers.



Figure 3. Variation of  $\eta 0$  as a function of CSDS for the four polymers studied. C = 1.5 wt%.

Figure 4 shows the variation of the steady-state viscosity  $\eta$  as a function of shear rate  $\gamma$  for B2 sample at different NaCl concentrations, in aqueous solution. From 0 to 0.2 mM of NaCl the

samples show a pronounced Newtonian behavior followed by a shear-thinning effect, from 0.3 to 0.5 mM the samples present a Newtonian behavior followed by a marked shear-thickening effect and finally a shear-thinning behavior. This shear-thickening effect is due to breakdown of the intramolecular associations and the formation of new intermolecular unions.



Figure 4. Variation of  $\eta$  as a function of  $\gamma$  for the B2 polymer at different NaCl concentrations. C = 1.5 wt%.

Figure 5 shows the n0 as a function of NaCl concentration (CNaCl) for the four polymers studied. It is observed that the addition of NaCl to samples B3 and B2 have the same behavior shown for the addition of SDS, i.e. the viscosity increased to a maximum followed by a decreased, this is possibly because at low NaCl concentrations, the molecules of this salt will be positioned in the middle hydrophobic junctions causing that the union is stronger, giving as result the increase in viscosity. Wang et al.[31] observed that the addition of salt at the appropriate level can enhance the viscosity of C18-modified PAA, due to the conformational changes and the enhanced interchain aggregation resulting from hydrophobic interactions. Upon the addition of NaCl, the polymer exhibits a transition from a nonaggregated to an aggregated polymer cluster, provides an electrostatic shield between charges along the polymer backbones. The polymer backbone contracts, which disrupts the intermolecular associative junctions, yielding smaller clusters with predominantly intramolecular association. The reduction in the active junctions has a significant impact on the rheological properties (decrease of viscosity), this behavior has been observed also for Tan et al. [32]. While the sample B1 shows a Newtonian behavior, i.e. no change in viscosity at all NaCl concentrations studied, this is possibly due to the low concentration of hydrophobic groups in the middle. Due that the behavior is the same shown for the addition of surfactant with hydrophobically modified polymers, the scenario can be the following (i) At low NaCl concentration, there is non-cooperative binding of the salt to the hydrophobic entities leading to the formation of both mixed unifunctional and plurifunctional aggregates. In a mixed unifunctional aggregate, only one hydrophobic entity or two entities belonging to the same

polymer molecule are incorporated. These mixed aggregates do not contribute to the high frequency elasticity of the system. A mixed plurifunctional aggregate contains several hydrophobic entities from different chains and therefore acts as a cross-link. The latter can be obtained either by a bridging effect of the salt onto several associating sequences initially isolated, or by binding of the salt onto a preexisting cross-link. In both cases, this leads to a strong enhancement of the viscosity of the system. (ii) At high salt concentration, the hydrophobic groups are saturated with salt and the excess of salt is localized in the aqueous medium resulting in the disruption of electrostatic repulsion of the polymer and the reduction of viscosity. While the B0 sample shows a decrease of viscosity when the NaCl concentration is increase, this is possibly due to that the polyelectrolyte does not contain hydrophobic groups, the salt instead of going to lie in the hydrophobic parts are dispersed in the aqueous medium to produce the breaking of the electrostatic repulsion and the decrease of viscosity.



Figure 5. Variation of  $\eta 0$  as a function of CNaCl for the four polymers studied. C = 1.5 wt%.

#### Conclusions

The systems investigated here are hydrophobically modified polyelectrolytes obtained by solution polymerization in which the hydrophobe content was varied. The influence in the rheological properties as a function of surfactant and salt concentration were investigated. The resultants of the interactions of polyelectrolyte with surfactant shown a typical behavior of associative polymers, with first an increase and then a decrease in the values of zero-shear viscosity. While for the case of the influence of salt, the polyelectrolyte which does not contains hydrophobic groups is observed a decrease in viscosity as the amount of salt is increased, this is due to breaking of the electrostatic repulsion present in the polymer, For polyelectrolytes containing hydrophobic groups have a surfactant-like behavior, i.e. the viscosity increases to a maximum followed by a decrease of it in function of the amount of salt, this can be attributed that the salt initially is localized in the hydrophobic groups present in the polyelectrolyte resulting in increased of viscosity, at high salt concentrations, the hydrophobic parts are saturated with salt and the excess of salt is dispersed in the aqueous medium to produce the breaking of the electrostatic repulsion and the decrease of viscosity.

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**BIOMATERIALS** 

## **RESPONSIVE GLYCOPOLYMERIC BIOMATERIALS**

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Macromolecular structures that are capable of selectively and efficiently engaging cellular targets offer intriguing approaches for mediating biological events. We have employed a combination of biosynthetic tools, bioconjugation strategies, and biomimetic assembly in the design of new materials for such applications.

In our early work, we have demonstrated that the interactions of heparin-modified glycopolymers with heparin-binding peptides and proteins can be used in the formation of hydrogels [1,2]. The release of growth factors from these materials, in response to cell-surface receptors, provides a novel mechanism for targeted delivery via delivery-mediated erosion, and has been demonstrated in vitro and in cell culture [2, 3]. We have also demonstrated the moderate changes in the elastic shear moduli of the heparinized materials cause marked differences in the adhesion and proliferation of cardiovascular cells [4], suggesting long-term, simple strategies for engineering desired therapeutic outcomes at select locations in vivo.

Our recent investigations have suggested the utility of elastomeric polysaccharide-binding polypeptides in cell encapsulation [5], as well as the promise of thiol-based adducts for controlling triggered hydrogel degradation and drug release. These materials may therefore be employed to develop a range of hydrogel-based therapies useful in cardiovascular applications.

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## POLYMER NANOFIBER CONSTRUCTS AS MATERIALS FOR REGNERATIVE MEDICINE AND MODELS FOR FUNCTIONAL BIOLOGICAL SYSTEMS

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Significant opportunities exist for the fabrication of materials having a useful biological function (e.g., enzyme activity) that are easily fabricated and utilized. Electrostatic polymer processing (e.g., electrospinning and electrospraying) has the versatility to meet these characteristics. Several classes of polymers, including biodegradable synthetics (e.g., PLGA), biocompatible but non-biodegradable synthetics (e.g., PVA, EVA) and natural polymers (e.g., collagen, fibrinogen) have been studied. We have been interested in fundamental understanding of electrospinning in cases of weak and strong polymer-polymer interactions in solution [1], and are now aiming to understand more complicated situations involving biopolymers such as collagen. Toward that end, recent work on collagen nanofiber electrospinning from benign solvents will be discussed [2] along with very recent studies of its application in wound healing using a mouse model. We have also begun to study nanofibrous polymers as models for functional biological systems, with special attention to the axon cortical layer and its cation-exchange properties. Toward that end, we have found that tubes of electrospun, highly-crosslinked poly(acrylic acid) [sodium salt] is responsive to calcium ions, exhibiting significant shrinkage that can be reversed with a chelator such as citrate. The prospect of fabricating an abiotic, polymeric mimic of an axon will be discussed.

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## POLYMERIC COATINGS FOR RETINAL PROSTHESES

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As chronic biomedical implants are expected to reside in the body for extended periods of time, the surrounding tissue needs to be protected from possible adverse effects exuded from the implant, and the implant itself needs to be protected from a potentially corrosive environment within the tissue. There is an added challenge when the implant is an electrically active device, such as a retinal prosthesis, and trace amounts of water can lead to electric device failure. We studied a variety of hermetic sealants and we developed chemistries for the ring-opening polymerization of N-carboxy anhydrides of amino acid using poly(ethylene glycol) or poly(oxazoline) as macro-initiators, resulting in block copolymers of the following structures: PEG-b-paa1-b-paa2 or PEG-b-paa1-co-paa2 and POX-b-paa1-b-paa2 or POX-b-paa1-co-paa2. The molecular weight of the block copolymers is strictly controlled and shows a monomodal molecular weight distribution.

We report here on different methodologies to generate dense polymer coatings on implant surfaces: (1) direct deposition of block copolymers, where the poly(amino acid) blocks constitute either a random copolymer of two amino acids or a block copolymer and (2) "on-the-surface-chemistry". Direct depositions were performed on solid Au-surfaces to study the impact of molecular weight and architecture and on Au-nanoparticles, which would be used on an actual implant. Secondly, PEG-b-paa and POX-b-paa polymeric micelles were produced, with functionalized PEG and POX chain ends forming the outer layer of the micelle corona. Poly(amino acid) "trunks" were single-pointedly attached to the substrate thus forming a densely packed coating, and subsequently decorated with the reactive polymeric micelles.

## NEW BIOBASED MATERIALS FROM RENEWABLE RESOURCES

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In agriculture, there is a fair amount of byproducts and waste materials. These materials typically contain significant portions of cellulose and hemicellulose. A good opportunity is to take advantage of these relatively cheap renewable resources and find uses for them in value-added applications. In this talk, several possibilities will be described.

A particular example will be given of the use of byproducts from cotton processing. A proximate analysis indicates that they contain about 30-31% cellulose, 17-18% lignin, 6-25% hemicellulose, and lesser amounts of protein and oil. Under suitable conditions, these byproducts are susceptible to chemical reactions. Thus, we have subjected them to iodine-catalyzed acylation reactions to produce cellulose acetate and other cellulose esters. Furthermore, we discovered that these cotton byproducts can swell in aqueous NaOH-isopropanol solutions at high pH, in which state they become susceptible to reaction with sodium monochloroacetate to form soluble carboxymethylated products.

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## NOVEL POLYESTER URETHANES WITH ENHANCED DEGRADABILITY AS POTENTIAL BIOMATERIALS FOR SCAFFOLD APPLICATIONS

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Immobilization of enzymes in general improves biocatalytic performance. Several studies on the immobilization of Yarrowia lipolytica lipase YLL onto different matrices have been made in the last years in the Polymer group of the University of Guanajuato. Immobilized lipases have proved to catalyze different oligomerization reactions, such as bulk ring opening polymerization of  $\varepsilon$ -caprolactone in the presence of different initiators. Biodegradable amphiphilic oligomers can be obtained by this methodology using isosorbide as initiator. [1] Lipases have been also used to produce PCL-diols (macrodiols) with controlled molecular weight. These macrodiols were used in turn to produce (by a chemo-enzymatic procedure) biodegradable polyester urethanes (PURs). [2]

Recently, this methodology was used to obtain aliphatic segmented thermoplastic polyester urethanes with hydrophilic character. Thermal and mechanical properties of the polymers depend mainly on the structure of macrodiol. In vitro degradation rates studies show that polymers degrade by a surface erosion mechanism. Cell-biological results indicate that obtained PURs are non-cytotoxic and haemocompatible in vitro and exhibited good biocompatibility in vivo. In that way, this type of PURs can be considered as excellent candidates for manufacturing of scaffolds to be used in tissue regeneration.

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## GLUCOSE/ISOSORBIDE BASED CHEMISTRIES: NOVEL THERMOPLASTICS, THERMOSETS AND ADDITIVES

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Glucose may be viewed as a chemical feedstock to produce new monomers, polymers and additives for a broad range of chemical intensive applications, including biomaterials. Isosorbide and its isomers are attractive because they as generally regarded as safe (GRAS), are a renewable resource and can be made readily available at competitive pricing. These moieties offer molecular geometry and chemical functionality compatible with many existing commercial chemistries. Applications ranging from the replacement of Bis Phenol-A in thermosets, the creation of new, high performance polyesters to the exploitation of the highly hydrophilic nature of some isosorbide derivatives in biomedical applications are under investigation. Of special interest is the impact of asymmetric reactivity, chirality and controlled stereochemistry in the design and performance of new, costeffective structures with commercial potential.

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## REACTIVE POLYMERS FOR CELL ENCAPSULATION AND EXTRA-CELLULAR MATRIX

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Our labs develop synthetic extracellular matrices, primarily for immuno-isolation of therapeutic cells. We recently described the formation of both core-crosslinked beads[1] and shell-crosslinked [2,3] capsules containing live C2C12 murine cells, and their transplantation into immunocompetent mice. Our approach to encapsulation is based on covalent reinforcement of cell-containing calcium alginate beads, by sequential coating with self-crosslinking polyelectrolytes. We recently showed that polycations such as poly-L-lysine, and polyanions containing electrophilic comonomers such as acetoacetate, anhydrides or activated esters, can self-assemble on alginate beads and spontaneously crosslink without need for small molecule reagents or photoinitiation. The resulting semipermeable hydrogel networks show excellent promise of protecting transplanted allogeneic cells from the host immune system.

This talk will describe the formation and properties of several types of hydrogel beads and capsules, including their internal structure (fluorescent microsopy), viability of encapsulated cells, and their interaction with the host immune system in mouse trials.

Access to such long-term immuno-isolating matrices is expected to be critical to clinical success of therapeutic cells currently being developed in a number of labs, including glucose-sensing insulinproducing cells derived from stem cells. We are also starting to explore the use of this polymer platform to study cell-cell and cell-extracellular matrix interaction.

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## BIDIMENSIONAL CELL GROWTH ON SEMICONDUCTOR POLYMERS SYNTHESIZED BY PLASMA

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#### Abstract

Polymers such as polyaniline, PAn, polypyrrole, PPy, the polyallylamine, PAlly, and polythiophene, PTh, may have semiconductor properties when are plasma polymerized and on the surface have functional groups as amines or sulfurs of the thiophene ring. This makes them suitable for testing in cell culture. Glass substrates coated with the four materials, PAn, PPy, PAlly, and PTh, were prepared Through the plasma polymerization technique, at powers of 15W, 30W and 50W and polymerization times of 15min and 30 min. These materials were characterized using standard techniques for polymers, SEM, FT-IR-ATR and Raman spectroscopy. Human hepatocyte cells, HepG2, were cultured on the substrates, with approximately  $1 \times 10^6$  cells per material. The cell culture was made for 11 days and photomicrographs of each sample were taken. The evolution of cell growth was followed in all materials (anchorage, reproduction and monolayer formation).

#### Introduction

The surface modification is one of the most widely used techniques to search for the biocompatibility of materials without altering their properties bulk. In our laboratory has obtained excellent results with pyrrole plasma coatings, both in implanted materials and in coating tissue engineering scaffolds[1-3]. Much of the success is associated with changing to a more hydrophilic surfaces and the introduction of amines on the surface.

Based on the experience in this work surfaces were coated with other polymers that can provide amines on the surface as allylamine and aniline, thiophene was also used to provide different functionality with its sulfur content, plasma polymerization was carried out under different conditions, since changing the electric field strength changes the chemical composition of the surface by the complexity of the plasma polymerization [4].

#### Experimental

#### **Polymer synthesis**

In a radio frequency plasma reactor at low pressure with insulated electrodes (see Figure 1) thin films were synthesized from different monomers: pyrrole (PPy), thiophene (PTH), allylamine (PAI) and aniline (PAn) at different conditions on the surface of conventional glass coverslip (Corning, 22 mm x 22 mm), cleaned with acetone and fixed on the lower electrode, the separation between the electrodes was adjusted to 1 cm, pressure in the reactor was decreased up to  $10^{-1}$  Torr, plasma was ignited at a power of 30 W and then adjusted the power to which took place the polymerization (15W, 30W, 50W), then the monomer was introduced to the reactor (pyrrole, thiophene , allylamine, aniline) continuously depending on the sample for 15 minutes or 30 minutes. After treatment, the reactor was turned off and kept closed for an hour in an atmosphere



of monomer before opening to atmosphere and removing samples.

Figure 1. Plasma reactor

## **Contact Angle**

To measure the contact angle a frontal photograph of the substrate with a drop of distilled water on the surface was taken with a digital camera. Once the digital photograph was taken, we measured the contact angle with the program ImageJ<sup>®</sup>. The procedure was repeated for each of the modified substrates.

#### **Infrared Spectra**

FT-IR spectra were sampled directly into the polymer deposited on KBr pellets (Potassium Bromide) introduced as substrates in the plasma reactor during polymerization, with a Perkin-Elmer 2000 FT-IR spectrophotometer with a wavelength between 4000 to 400 cm-1 and 32 scans.

## **Cell Growth procedure:**

1. Polymerized materials were placed in 12 culture dishes of 35 mm.

2. 2 ml ( $5x10^5$  cells/ml) of HepG2 cells were added with growth medium.

3. The cell medium was changed every other day for 18 days.

4. The cells were cultured at a temperature of 37°C with 5% CO<sub>2</sub> and saturated humidity.

5. Cell proliferation was evaluated on the coverslips on days 2, 4, 8, 11, 14 and 18 of culture, with an inverted microscope.

## **Results and Discussion**

The characterization by contact angle showed that a change occurred on the coverslip surface of the substrates used, where it is important to note that for all the monomers used in the polymerization angles less than 90  $^{\circ}$  were obtained, so that all surfaces tend to be hydrophilic, which contributes to the anchorage of the cells. Surfaces with smallest angle were allylamine with 30W-15min and 30W-30min and the highest contact angle was thiophene with 30W-30min.



Figure 2 shows the measurement of contact angles for different polymerization conditions, the contact angle of pyrrole increases with increasing power but shows no significant change when you hold the power and polymerization time increases, this happens because when you increase the power, monomer rings are destroyed and this gives the surface a more hydrophobic composition, however when time increases more rings are not destroyed. In the case of thiophene we have the reverse effect, the increase in power does not produce more hydrophobic radicals, but increasing the time, the surface becomes more hydrophobic. The allylamine gives us more hydrophilic surfaces and is only affected by time. Surfaces treated with aniline are more hydrophobic than those of thiophene implying that more monomers are destroyed and this destruction results in a more hydrophobic chemical composition.



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By means of FTIR, the presence of PPy, PTh, PAlly and PAn was established, characteristic absorption bands were identified, such as those found between 3500-3300cm<sup>-1</sup> showing the presence of NH bonds as part of the molecule pyrrole, NH and NH2 bonds of the molecule of aniline, absorptions of NH2 (3425 cm<sup>-1</sup>) as part of the molecule of allylamine. Two absorption bands at 3459 and 2950 cm<sup>-1</sup> which can be assigned to the links-C = CH and CH respectively, the latter produced by the destruction of the rings.

## **Cell Culture**

We performed in vitro cell growth and it was studied on the substrates polymerized at different times and power, presenting cell adhesion and proliferation of human hepatocytes, influenced by the power and polymerization time applied.

It is important to note that the deposited films are not toxic because it was obtained cell adhesion and growth on the surface of the substrates, the cells grew in all the films and only in the thiophene it was observed that growth tended to form inhomogeneous agglomerates and took to long to reach confluence.



Figure 3 shows the materials that showed better results for adhesion and cell proliferation: a)Pyrrole30W-30min,b)Thiophene15W-15min,c)Allylamine30W-15min,d)Aniline 30W-15min.

For coatings made of PPy it was observed that for the ones made at small power (15W) the surface is fractured when they are in the culture medium, PTh coatings suffer fractures for all powers and polymerization times, in the case of PAlly the high power (50W) cause wrinkles in the material surface and fractures in contact with the culture medium, the PAn coating material have fractures for small power (15W-15min).

#### Conclusions

The obtained result can be regarded as satisfactory since the materials surface modified by plasma were shown to have good interaction and behavior at the cellular level (biocompatibility and adhesion), so that the obtained materials have the potential to be used as a coating of scaffolds in tissue engineering.

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# Synthesis and Characterization of Polyphosphazenes Modified with Hydroxyethyl-Methacrylate and Poly(Lactic Acid)

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## ABSTRACT

Poly(dichlorophosphazene) was prepared by melt ring-opening polymerization of the hexachlorocyclotriphosphazene. Poly[bis(2-hydroxyethyl-methacrylate)-phosphazene] and Poly[(2-hydroxy-ethyl-methacrylate)-graft-poly(lactic-acid)-phosphazene] were obtained by nucleophilic condensation reactions at different concentrations of the substituents. The properties of the synthesized copolymers were assessed by FTIR, <sup>1</sup>H-NMR and <sup>31</sup>P-NMR, thermal analysis (DSC-TGA) and electron microscopy (SEM). The copolymers have a block structure and show two  $T_g$ 's below room temperature. They are stable up to a temperature of 100°C. The type of the substituents attached to the PP backbone determines the morphology of the polymers.

## Introduction

Polyesters, polyorthoesters, polyanhydrides, poly(R-amino acids), and polyphosphazenes are degradable polymers that have been investigated for a variety of biomedical applications such as sutures, drug delivery systems and scaffolds for tissue engineering [1]. Useful properties can be obtained by blending two different polymers. However compatible polymer blends require strong molecular interactions between polymer chains [2].

Poly(organophosphazenes) offer an appealing platform for the design and synthesis of novel biodegradable polymers as well as critical advantages for the design of biologically functional macromolecules with a broad structural diversity [3] high functional density, and tailored biodegradability [4]. These polymers are of scientific and technological concern since the first work of synthesis reported by Allcock [5, 6].

Polyphosphazenes, PP, posses special characteristics, including flame-retardant properties, high resistance to oil and solvents, and feasibility for tailored properties according to the choice of organic, inorganic or organometallic side groups [7]. As biomaterials they have inherent advantages, due to their biocompatibility and fast degradation rate. In addition, degradation residues, phosphate, ammonia, and side groups, are either non-toxic when they are present in small quantities or are easily metabolized by the human body [8, 9].

Polyphosphazenes are hybrid polymers with a flexible inorganic backbone of alternating phosphorus and nitrogen atoms and organic side groups. Their molecular weights vary from 3 to 10,000 (-N=P-) repetitive units having two substituents (-R) attached to the phosphorus atom [7]. Polyphosphazenes are synthesized by reactions with alkoxydes, aryloxides, or amines from a highly reactive macromolecular intermediate, poly(dichlorophosphazene), prepared by thermal polymerization which is ring opening of hexachlorocyclotriphosphazene (HCCP) at 250°C. The chlorine atoms can be further replaced via nucleophilic substitution; using amino acid ester, imidazolyl, glyceryl, or glycosyl side groups that are also hydrolytically sensitive [5].

The flexible inorganic backbone of the poly(phosphazene) structure plays an important role in tissue regeneration. It can be modified with ester, anhydride, and unsaturated groups to improve chemical stability and mechanical properties. Co-substituted poly(organophosphazenes) with unsaturated side groups are used to prepare interpenetrating polymer networks with acrylonitrile, styrene, acrylic acid, and methyl methacrylate, using sequential interpenetrating methods. Such polyphosphazenes can be readily crosslinked either by exposure to heat or to ultraviolet light [10].

In this work Poly[(2-hydroxy-ethyl methacrylate)-graft-poly(lactic acid)-phosphazene] and Poly[bis(2-hydroxyethyl-methacrylate)-phosphazene] were synthesized by condensation polymerization reactions.

The 2-hydroxyethyl methacrylate (HEMA) was selected to improve biocompatibility and bifunctionality. HEMA was firstly attached to the side chain along with glycine-ethyl ester to form a precursor with the unsaturated substituents. HEMA is used for prosthesis, teeth and bones reconstructive materials, and it is frequently mixed with acrylic polymers, like Bisphenol-A-glycidyl-dimethacrylate (Bis-GMA), in photo-polymerizable dental resins. HEMA is intended to infiltrate the demineralised dentin and prevent collagen collapse [11]. HEMA melts at about  $-12^{\circ}$ C.

The Poly(lactic acid), PLA, was selected because it is a thermoplastic biocompatible and biodegradable material with good mechanical properties, and its biodegradation products, mainly lactic acid, are also non toxic nor cancerigenous to the human body [5, 12]. The PLA chemistry involves the processing and polymerization of lactic acid monomer. Lactic acid (HOCH3CHCOOH) is a simple chiral molecule which exists as two enantiomers, L-and D-lactic acid. The polymer is relatively hard, with a glass transition temperature between  $60^{\circ}$ C and  $70^{\circ}$ C and a melting point between  $170 - 180^{\circ}$ C.

## Experimental

All materials used here were chemical grade. HEMA and LA were distilled just before use. Hexachlorocyclotriphosphazene, HCCP, was purified twice by sublimation. Poly(organophosphazenes) nucleophilic substitution scheme reaction is shown in Figure 1. The Poly(dichloroposphazene), PP, was obtained by melt ring-opening polymerization of HCCP under vacuum at 250°C for 3h. Typical PP-FTIR bands were observed at 1215 and 748 cm<sup>-1</sup>, <sup>31</sup>P-NMR peak at -16.1 ppm. The methods of polymerization and substitution reactions to obtain PP-HEMA and PP-HEMA-PLA are described elsewhere [13].



Figure 1. Scheme of the synthesis of poly(organophosphazenes).

## **Results and Discussion**

PP-HEMA was obtained at two molar ratios: 1:3 and 1:6. The characteristic IR bands (cm<sup>-1</sup>) of the phosphazene backbone are: 2947 (CH<sub>2</sub>), 1720 (C=O), 1625 (C=C), 1473 (CO-O), 1033 (P-O-C), 1168, and the <sup>31</sup>P-NMR peaks: 1.5 ( $\delta$ =ppm); <sup>1</sup>H-NMR <sub>HEMA</sub>[13] at 6.0 (1H), 5.4 (1H), 4.3 (2H), 2.0 (3H), 1.7 (2H) ( $\delta$ =ppm).

The synthesis of PP-HEMA-PLA involves chemical linking of HEMA and LA to the polymer backbone and graft polymerization [14]. The typical IR bands (cm<sup>-1</sup>) were: 3452 (polymeric -OH), 2947 (CH<sub>2</sub>), 1745 and 1724 (C=O), 1625 (C=C), 1477 and 1150 (CO-O), 1037 (P-O-C), 1172 (phosphazene backbone), and the <sup>31</sup>P-NMR peaks: 1.5 and 0.6 ( $\delta$ =ppm); <sup>1</sup>H-NMR<sub>HEMA</sub>, 6.0 (1H), 5.4 (1H), 4.3 (3H), 2.0 (2H), 1.7 (2H) ( $\delta$ =ppm); as well as <sup>1</sup>H-NMR<sub>PLA</sub> peaks: 1.3 (3H) 3.5 (1H) 12 (1H) ( $\delta$ =ppm). For the PP-HEMA-PLA an additional FTIR peak can be observed at 3452 cm<sup>-1</sup> corresponding to the polymeric alcohol and at 1745 cm<sup>-1</sup> to the carboxylic group of PLA [12, 14-16].

The structure of PP, PP-HEMA-1:3 and PP-HEMA-1:6 were analyzed by  ${}^{31}$ P-NMR. The PP spectrum shows a peak at -16.1 ppm corresponding to low molecular weight  $[P(Cl_2)=N]_n$  [17], while the polymers PP-HEMA-1:3, PP-HEMA-1:6 and PP-HEMA-PLA shows a peak at 1.5 ppm to the modified phosphazene  $[P(OR)_2=N]_n$ . In addition, the PP-HEMA-1:3 shows a peak at 20 ppm which is assigned to six atoms ring; when the HEMA ratio was increased to 6 mmol a complete chlorine substitution was obtained. For PP-HEMA-PLA another peak appears at 0.6 ppm assigned to the substitution of chlorine by PLA.

The thermal transitions of the polymers were determined by DSC. The obtained data indicate that all polymers are flexible above 0°C. PP showed a single  $T_g$  at -90°C while both PP-HEMA and PP-HEMA-PLA have two  $T_g$ 's: (a) for PP-HEMA-1:3 -71°C and - 6.6°C; (b) for PP-HEMA-1:6 -67°C and -7.5°C; and (c) for PP-HEMA-PLA -75°C and - 15°C. The lowest  $T_g$  value shown by each copolymer corresponds to the PP backbone.

The  $T_g$  of PP-HEMA-PLA at -15°C corresponds to the PLA grafted on the PP backbone. The  $T_g$  of PP-HEMA at about -7°C is attributed to the HEMA chemically attached to the PP backbone. The observed  $T_g$  temperatures are similar to those reported elsewhere [14, 18].

The thermal stability of the polymers was analyzed by TGA. PP lost about 5% of weight between 50°C and 100°C due to residual monomer evaporation. Between 200°C and 300°C there is another 5% loss of weight, which is attributed to the elimination of chlorine. Above 300°C the PP degrades fast. PP-HEMA and PP-HEMA-PLA are quite stable up to 100°C. The stability of PP-HEMA increases with the content of HEMA attached on PP because of the good thermal stability of HEMA [19 Zhou]. In PP-HEMA-PLA the decomposition temperature of PLA starts at 109°C [20 Lima]. Excluding monomer evaporation in PP, its thermal stability is greater than that observed in the copolymers.

The surface of the polymers was examined by SEM (Figure 2). The PP shows a semiuniform surface while the copolymers show distinctive characteristics. PP-HEMA-1:3 and PP-HEMA-1:6, show a rod like microstructure that is enhanced as the concentration of HEMA increases. PP-HEMA-PLA shows a rod structure embedded in a continuous film. Thus morphology depends on the type of the substituents attached to the PP backbone [21].



Figure 2. SEM images: (a) PP, (b) and (c) PP-HEMA at 1:3 and 1:6 and (d) PP-HEMA-PLA

## Conclusions

Poly(dichlorophosphazene) was prepared directly by melt ring-opening polymerization of hexachlorocyclotriphosphazene. This polymer was useful for the design and synthesis of Poly[(2-hydroxy-ethyl-methacrylate)-graft-poly(lactic-acid)-phosphazene] and Poly[bis(2-

hydroxyethyl-methacrylate)-phosphazene] by ring opening polymerization reactions, at substituents. different concentrations of the The chemical structure of Poly(dichlorophosphazene), poly[(2-hydroxy-ethyl-methacrylate)-graft-poly(lactic-acid)phosphazene] and Poly[bis(2-hydroxyethyl-methacrylate)-phosphazene] were determined by FTIR, NMR and DSC. All polymers are flexible above 0°C and are thermally stable up to  $100^{\circ}$ C. The morphology of the polymers depends upon the type and concentration of the substituents attached to the PP backbone.

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## NOVEL GRADED SCAFFOLDS, METHODS OF FABRICATION AND APPLICATIONS FOR BONE TISSUE ENGINEERING

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#### Abstract

New processes were developed for fabrication of realistic scaffolds for use in bone tissue engineering, i.e., twin screw extrusion, twin screw extrusion and spiral winding, twin screw extrusion and electrospinning and co-extrusion. Scaffolds were fabricated with interconnected porosity from poly(caprolactone), incorporated with concentration distributions of nanoparticles of hydroxyapatite and ß-tricalcium phosphate for osteo-conductivity and various bioactives for cell proliferation and differentiation. The scaffolds generated with the four different methods could all be graded with respect to the porosity, pore size, distributions of the concentrations of bioactives and mechanical properties in both the axial and radial directions to allow better mimicry of the complex elagance of native tissues. Tissue constructs were generated by seeding the scaffolds with preosteoblasts or stem cells derived from bone marrow and adipose tissue. In vitro experiments involving cell growth and migration, histology and mechanical properties revealed that the PCL scaffolds can be suitable for repair of critical-sized bone defects and arthrodesis for spinal fusion applications.

## Introduction

Repair of large segmental bone defects, i.e., critical-sized defects, which occur due to blunt trauma, tumor resection surgeries, pathological degeneration and congenital deformities, are challenges for orthopedic surgery [1-4]. Currently, about 5-10% of procedures applied to repair critical-sized defects result in delayed unions or non-unions [1-2]. Autografting is still the "gold standard" in clinical bone repair procedures [3,5-7]. However, up to 30% of the autografting procedures have complications associated with the donor-site morbidity, limited tissue availability, varying quality and longer hospital stays [6-8]. Other alternatives, i.e. allografts and xenografts, suffer from limited sources of supply, contamination risks, immunogenic incompatibility and inability to incorporate with the host bone [3,7,8]. Designing synthetic bone grafts offers an alternative route in treatment of critical-sized defects [1-8]. Clinical trials have demonstrated the possibility of using metallic, ceramic and polymeric bone graft substitutes [5,9-14]. It is generally understood that the bone grafts need to be (i) biocompatible, (ii) preferably bioresorbable to prevent second surgery for removal after full recovery or due to late immunologic response, wear or dislodgement, (iii) mechanically adequate and stable until functional bone tissue forms within the defected area, and (iv) most importantly osteoconductive and preferably osteoinductive [1,6-8,12].

A second approach, i.e., bone tissue engineering, attempts to utilize porous polymeric scaffolds which are typically seeded with patient's own stem cells. Tissue constructs are formed upon the proliferation and differentiation of the cells on the scaffold within a bioreactor and implanted to

defect site. Typical polymeric materials for such tissue engineering scaffolds are polyglycolide, polylactide, polycaprolactone (PCL) and their copolymers or their biocomposites with particles like hydroxyapatite and tricalcium phosphate as well as other bioagents like growth factors [6,7,9-14].

The designing and fabrication of bioresorbable polymeric bone graft substitutes and porous scaffolds for tissue engineering are both challenged by the complex structural and compositional gradations found in human tissues [15,16]. For example, it would be desirable for the bone graft substitutes used in the repair of critical sized defects in long bones like femur and tibia to accommodate their changing porosities and moduli along their transverse and axial directions [17,18]. Therefore, mimicking of such complex gradations found in native tissues can require correspondingly complex gradations in bone graft substitutes and tissue engineering scaffolds which exhibit tailored three-dimensional distributions in composition, structure and properties. However, past efforts to generate bone graft substitutes and scaffolds with such gradations were constrained by the available conventional scaffolding methodologies. Conventional methods of generating graded scaffolds include layer-by-layer casting, freeze-drying, phase separation, and rapid prototyping techniques including fused deposition modelling, 3D printing, selective laser sintering, and stereolithography [15,16]. However, none of these methodologies are sufficiently flexible to allow the reproducible and industrially-scalable grading of bone graft substitutes and scaffolds for a wide range of compositions, porosities and mechanical properties.

Twin screw extrusion based technologies can be applied to the fabrication of radially and axiallygradable porous structures from bioresorbable polymers and osteoconductive additives targeting bone tissue repair and regeneration. These technologies that we have demonstrated include twin screw extrusion, TSE, alone, TSE in conjunction with spiral winding, TSE with electrospinning and co-extrusion. The fabrication of the graded structures was demonstrated here using PCL and biocomposites of PCL with HA and TCP and PCL incorporated with insulin and ßglycerophosphate [19-24]. The co-extrusion based graded scaffold fabrication was demonstrated via bone graft substitutes which consist of an outer stiff layer of PCL incorporated with HA/TCP and a softer core layer from PCL. The outer layer exhibits lower porosity and smaller pore sizes, and the softer core layer exhibits higher porosity and larger pore sizes (inspired from cortical/cancellous bone). The interconnected nature of the porosities of the inner and outer layers should allow cell migration and exchange of nutrients and metabolic wastes in the radial direction during bone regeneration [25]. Furthermore, the bioresorbable bone graft substitutes are also graded in the axial direction. This was primarily by tailoring the concentration of the HA/TCP used in the fabrication of the outer layer as a function of axial distance to give rise to a relatively long bone graft substitute that is progressively stiffer in the axial direction.

## Experimental

## Novel methods of graded scaffold fabrication

The four methods of scaffold fabrication are illustrated in Figure 1.



Figure 1. Different methods of graded scaffold fabrication developed at Stevens Institute of Technology

In twin screw extrusion and spiral winding the extrudates, the composition and porosity of which can be altered as a function of time are wound on a simultaneously translating and rotating mandrel to generate radially and axially graded scaffolds. Some examples of radial gradations of porosity are shown in Figure 1 [21,22]. Figure 1 also shows the twin screw extrusion process applied concomitantly with electrospinning to generate nanofibrous meshes which can be graded with porosity, pore size and bioactive concentration distributions [19,20,23]. The two bioactives used in the demonstration study for TSE-electropinning were  $\beta$ -gloycerophosphate and insulin. The regions that are rich in insulin were determined to give rise to chondrocytic differentiation of adipose-derived stem cells, whereas the regions that were rich in ß-gloycerophosphate were determined to furnish greater degree of mineralization [23]. The other method that was applied to generate axially and radially graded scaffolds of PCL is the co-extrusion method that was demonstrated to generate distributions of porosity, pore size and concentration distributions of TCP and HA in both the axial and radial directions (cage/core structures). The modulus of the coextruded scaffolds could be manipulated systematically in both the radial and axial directions. When tissue constructs were generated by seeding bone marrow derived stem cells onto the coextruded graded scaffolds and samples were harvested as a function of time during cell proliferation and differentiation in media, the gene expression levels and µ-CT analysis revealed the osteogenenic differentiation, bone ECM formation and mineralization as affected by the gradations of the bioactive ingredient, i.e., HA and TCP concentrations [26].

### Conclusions

A series of novel fabrication methods were developed to better provide the means to generate graded scaffolds from a bioresorbable polymer, PCL, and biocomposites of PCL with osteoconductive particles of tricalcium phosphate, TCP, and hydroxyapatite, HA. These fabrication methods included twin screw extrusion, twin screw extrusion in conjunction with spiral winding and twin screw extrusion with electrospinning and co-extrusion.

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## SYNTHESIS OF BIODEGRADABLE SEGMENTED POLYURETHANES FOR BONE TISSUE REGENERATION

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## Abstract

Segmented polyurethanes (SPU) are polymeric biomaterials with a long history of medical use and although the main area of application is the cardiovascular field, they have also been suggested for bone tissue regeneration. In this regard, they have been used as elastomer [1], as composites with  $\beta$ -TCP [2], Bioglass [3] or by increasing the rigid segment content [4]. More recently, our group has reported the use of either L-glutamine or ascorbic acid as chain extenders in combination with PCL and HMDI [5]. In this study, we present the results obtained with segmented polyurethanes prepared with an aliphatic biodegradable diisocyanate (dimeril diisocyanate), polycaprolactone and  $\beta$ -glycerol phosphate (BGP). Their physicochemical and mechanical properties were evaluated by FTIR, DSC, TGA, DMA, XRD, SEM and tensile mechanical testing. Their accelerated biodegradation was studied in acidic (HCl), alkaline (NaOH) and oxidative (H<sub>2</sub>O<sub>2</sub>, NaClO) media and compared with an SPU prepared with butanediol (BD). FTIR showed typical bands for polyurethanes at 3390 cm<sup>-1</sup> (NH), 1735 cm<sup>-1</sup> (C= O), 1529 cm<sup>-1</sup> (C-N) although P-O absorptions from  $\beta$ -glycerol phosphate were not clearly observed. The crystalline structure of the SPU with BGP was observed by DSC (Tm=40.8 °C  $\pm$  1.6°C) and by XRD (2 $\theta$  =21.4° and 23.6°) and assigned to the PCL. The Tg of the soft segment, obtained by DMA, was observed at -12.9±2.8°C for those SPUs prepared with BGP but at -20.8±1.2°C for those containing BD. Two decomposition temperatures (Td1=411°C y Td2=516.1°C) were observed by TGA for BGP and BD containing SPUs. These polyurethanes showed elastomeric behavior (183%) while SEM showed a granular surface (50-100 µm diameter) in both polyurethanes. These polymers degrade more under acidic and alkaline conditions than oxidative media.

## Introduction

Segmented polyurethanes (SPU) are polymeric biomaterials with a long history of medical use and although the main area of application is the cardiovascular field, they have also been suggested for bone tissue regeneration. In this regard, they have been used as elastomer [1], as composites with  $\beta$ -TCP [2], Bioglass [3] or by increasing the rigid segment content [4]. More recently, our group has reported the use of either L-glutamine or ascorbic acid as chain extenders in combination with PCL and HMDI [5].

For tissue engineering purposes, biodegradable SPUs can be prepared either using biodegradable soft segments or biodegradable rigid segments. In the first case, polyester based polyurethanes such as those based on PCL have been prepared [6,7] in addition to PLA- [8], PEO- [9,10] and poly(3-hydroxybutyrate diol)- [11] based SPUs. On the other hand, as the rigid segment is formed by the diisocyanate and the chain extender, there are two possibilities for preparing biodegradable polyurethanes: the diisocyanate can be modified or the chain extender can be chosen from a variety of important biological molecules. In this way, SPUs with biodegradable rigid segments
have been prepared with aliphatic diisocyanates such as 1,4-butanediisocyanate (BDI) [6], ethyl lysine diisocyanate (ELDI) [7], hexamethylene diisocyanate (HDI) [12], methyl lysine diisocyanate (MLDI) [13] among others. In terms of the chain extender, various amino acids have been used [12-17] and other low molecular weight compounds with a specific functionality or activity [18].

In this study, we present the results obtained with segmented polyurethanes prepared with an aliphatic biodegradable diisocyanate (dimeril diisocyanate), polycaprolactonediol, also a biodegradable polyester type macrodiol and  $\beta$ -glycerol phosphate (BGP) which is found in osteogenic culture media in addition to glutamine and ascorbic acid.

## Experimental

#### Segmented polyurethane synthesis

SPU's with a molar ratio of 2:1:1 (DDI:PCL:BGF or BD) were prepared in a two steps reaction. The prepolymers were obtained by the reaction of poly( $\epsilon$ -caprolactone)diol (PCL,Mn=2000, Aldrich) with an excess of dimeril diisocyanate (DDI 1410, Cognis). Then, chain extension was conducted with  $\beta$ -glycerol phosphate (BGP, Aldrich). For comparison purposes, a segmented polyurethane was prepared using butenediol (BDO, Aldrich) as chain extender. The chemicals used are shown in Figure 1. The SPU's were abbreviated as SPUBGP121 and SPUBDO121 respectively.



Figure 1 Chemical structure of the reagents used for the SPU synthesis

#### Segmented polyurethane characterization Spectroscopic studies

FTIR spectra of the SPU's were obtained from thin films deposited onto KBr disks after evaporation of their THF solutions using a Nicolet Protegé 460 spectrophotometer. Spectra were recorded from 4000 to  $400 \text{ cm}^{-1}$ , averaging 100 scans with a resolution of 4 cm<sup>-1</sup>.

## Thermal characterization

Decomposition temperatures at peak (Td) were obtained by thermogravimetric analysis using a TGA 7 from Perkin Elmer. 5 mg were heated from 45°C to 650°C at a heating rate of 5°C/min under nitrogen atmosphere. Differential Scanning Calorimetry was used to determine the melting point on the SPU's using a Perkin Elmer DSC 7. In this case, 5-7 mg of the sample was heated from 0°C to 150°C at 10°C/min under nitrogen atmosphere. Dynamic mechanical analysis as a function of temperature was conducted using a DMA 7 from Perkin Elmer in the extension mode. Rectangular specimens of 20x3x0.1 mm from SPU's were subjected to a static force of 60 mN and a dynamic force of 40 mN at 1 Hz. Storage modulus and Tan  $\delta$  were determined in the temperature range between -100 °C to 150 °C at a heating rate of 5 °C/min.

#### **Microstructure Determination**

The microstructure of the nanocomposites was observed by SEM using a Jeol 6310 LV. An accelerating voltage of 20 kV was used and the samples were coated with gold. X ray diffraction measurements were carried out with a D-5000 Siemen diffractometer (Karlsruhe, Germany) using monochromatic radiation (CuK $\alpha$   $\lambda$ =1.5418Å) at 35 kV and 24 mA. The samples were registered in the range 5°<2 $\theta$ <60° with a step count of 3s and a step size of 0.02° (2 $\theta$ ). For these experiments 1 cm<sup>2</sup> films were used.

#### **Mechanical Properties**

Tensile tests were carried out in a Shimadzu AG-I universal testing machine using a cross-head speed of 50 mm/min according to ASTM D-412. We report the ultimate tensile strength ( $\sigma$ ), strain at break ( $\epsilon$ ) and modulus (E).

#### Accelerated degradation

Accelerated degradation was studied in acidic (2N HCl), alkaline (5 M NaOH) and oxidative (30%  $H_2O_2$  and NaClO) media by placing a known amount of the SPUs under reflux during 24 h.

#### **Results and Discussions**

Figure 1 shows the FTIR spectra for the synthesized polyurethanes. Typical bands were observed at 3390 cm<sup>-1</sup> due to NH stretching, at 1735 cm<sup>-1</sup>(C=O) due to PCL and urethane linkage and at 1529 cm<sup>-1</sup> due to C-N bonds. However, P-O absorptions were not clearly observed in the polyurethane prepared with BGF.

The crystalline structure of the SPU with BGP was observed by DSC (Tm=40.8 °C  $\pm$  1.6°C) and by XRD (2 $\theta$  =21.4° and 23.6°) and attributable to the PCL (Figures 2a and 2b respectively). SPU's containing BGF showed a single broad melting peak during the first and second heating. However, those prepared with BDO showed two peaks during the first heating trace and a single endotherm during the second heating suggesting a different crystallization of the PCL in the polyurethane. XRD also showed additional reflections for the polyurethane prepared with BDO.

The Tg of the soft segment, obtained by DMA, was observed at  $-12.9\pm2.8^{\circ}$ C for those SPUs prepared with BGP but at  $-20.8\pm1.2^{\circ}$ C for those containing BDO. These results suggest more interactions of the soft segments with the rigid segments for BGF containing polyurethanes.

Two decomposition temperatures (Td1=411°C y Td2=516.1°C) were observed by TGA for SPUBGP121 which were very similar for BDO containing SPUs. However, in these systems is not easy to assign Td to either the rigid or the soft segment as both are decomposing simultaneously.



Figure 1 FTIR spectra of segmented polyurethanes. SPUBGF121 (top) and SPUBDO121 (bottom)







Figure 3 DMA thermograms of SPUBGF121 and SPUBDO121. Storage modulus (a) and Tan  $\delta$  (b)

a)



**Figure 4** TGA thermograms of SPUBGF121 and SPUBDO12. Mass loss (a) and first derivative (b)

Polyurethanes prepared with  $\beta$ -glycerol phosphate showed elastomeric behaviour (183%) and slightly higher ultimate tensile strength (1.9 MPa) but slightly lower modulus (21.1 MPa) than SPUB's containing butanediol (E=1.1 MPa,  $\sigma$ =21.5 MPa,  $\epsilon$ =6.6%). SEM showed a granular surface (50-100  $\mu$ m diameter) in both polyurethanes. These structures can be related to the presence of PCL, where the grain size tends to be bigger in the SPU's prepared with butanediol. These polymers degrade more under acidic and alkaline conditions expecting caproic acid as the main degradation product.



Figure 5 SEM surface micrographs of SPUBGF121 (a) and SPUBDO12 (b).

## Conclusions

Polyurethanes containing  $\beta$ -glycerol phosphate were succesfully prepared in a two step solution polymerization. These semicrystalline polymers exhibited good mechanical properties but not comparable to either cortical or cancellous bone. However, due to their potential of biodegradation (as demonstrated by their accelerated degradation) and the potential release of osteogenic molecules ( $\beta$ -glycerol phosphate) they can be used in bone tissue regeneration. Furthermore, their mechanical properties can be tailored to be similar to bone by increasing the content of rigid segments.

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## RADIATION-GRAFTING OF STIMULI RESPONSIVE COPOLYMERS FOR BIOMEDICAL APPLICATIONS

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Gamma-radiation grafting technique has many advantages over other conventional methods since it is a simple, efficient, clean and environment-friendly process. It usually allows combining the synthesis and sterilization in a single technological step under easily controlled conditions. Thus, irradiation is a very convenient method for the surface grafting of smart polymers onto medical devices. In the last years, there has been a remarkable growth in the research and development of synthetic polymers for biomedical components. Stimuli-responsive polymers that are able to modify their properties in response to changes of environmental factors have attracted a great attention. When the responsiveness is predictable and reversible, the stimuli-responsive systems are termed "smart" or "intelligent". Smart systems can be designed to respond to a wide range of external variables or physiological/pathological conditions, such as temperature or pH. Particularly, surface-grafted responsive networks can endow medical devices with stimuli-controlled loading and release of antimicrobial and anti-inflammatory agents for prophylactic or therapeutic purposes. In this contribution, examples of the work carried out by our group regarding the modification of polymeric films (PP, LDPE, PTFE or silicone rubber) by gamma-radiation grafting of pH and thermo sensitive components (NIPAAm, DMAEMA, AAc), using either pre-irradiation or direct method, and their biomedical applications are presented.

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# CHITOSAN SCAFFOLDS FOR TISSUE ENGINEERING

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#### Abstract

Perforation of tympanic membrane, that causes chronic infections and hearing loss, can be surgically repaired by the use of a chitosan implant to seal the perforation thanks to its excellent biocompatibility properties. To modify and to control microstructural and physicochemical aspects of chitosan, several crosslinking agents were are used to obtain crosslinked chitosan membranes: glutaraldehyde, triethylene glycol and functionalized polyethylene glycols into glycol diglycidil ethers. It was found that the functionalized polyethylene glycols allowed tailoring the mechanical properties of the chitosan membranes by increasing the % of elongation at break as the size of the functionalized polyethylene glycol was incremented. Porosity and water absorption were reduced by the introducction of chemical crosslinks. Further characterization of the thermal and mechanical properties of the membranes is also presented. Biocompatibility studies showed that the glycol diglycidil ethers are promising candidates to be used as crosslinkers to obtain biocompatible insoluble chitosan patches. Trial tests have begun for soluble chitosan patches to repair perforated tympanic membranes. It was analyzed their capacity for bio-integration into perforated eardrums in New-Zealand adult rabbits, and the consequent functional restoration, compared with the traditional muscle fascia. The histological analysis reveals an increased thickness of the membranes for chitosan patches along with higher number of fibroblasts compared with controls. Hence, we conclude that the soluble chitosan patch substitute of the soluble chitosan patch subs

#### Introduction

Perforation of tympanic membrane (TM) is the common result of chronic otitis media. This situation may evolve into chronic infections and hearing loss. Even though TM is able to regenerate and to repair by itself, the process may become lengthy and it would be desirable to surgically repair the TM by the use of an implant to seal the perforation. Several methods have been reported to such effect, including the very early works using pig's bladder moving forward to the more recent ones using natural materials such as paper patches or muscle fascia autografts and synthetic ones such as gelfoam and alloderm[1-5]. In the past 15 years there have been several studies using chitosan as biomaterial to repair damaged tissues[6-8]. Recently, it has been used in tympanoplasty[9, 10]. Chitosan membranes (CM) have been prepared by several methods and techniques to achieve particular characteristics desired in biomedical applications. Choosing a particular membrane is related to the manufacturing process since many of the physical characteristics are defined there. An useful technique to obtain CM is the process of phase separation[11]. Crosslinking has been used to enhance stability and mechanical properties of CM. Typical crosslinkers reported in the literature are glutaraldehyde (GA), hexamethylene diisocyanate and epichlorhidrine[12, 13]. The crosslinked CM obtained using such crosslinkers are usually rigid and not suitable for middle ear surgery. In this work, it is reported for the first time the crosslinking of CM with different glycol diglycidil ethers (GDE) made of tryethylene glycol (TEG) or commercially available polyethylene glycols (PEG) of different molecular weigths and the characterization of the crosslinked CM. They are also presented results for CM

uncrosslinked and for CM crosslinked with GA for comparison purposes. Finally, it is presented relevant features of the use of CM as chitosan patches in tympanoplasty of New-Zealand adult rabbits (NZAR)

# Experimental

## **Polymer synthesis**

Chitosan solutions were mixed with functionalized glycols that act as crosslinkers such as GDE made of TEG or commercially available PEG (Pluracol E400 and Pluracol E4000). The GDE were synthesized at our lab by a modification of the method reported by Gu[14]. The prepared chitosan mixtures were poured into rectangular molds and dried under vacuum at 60°C to obtain membranes. Finally, the CM were neutralized and dried again under vacuum at room temperature. CM were characterized in terms of porosity, water retention, scanning electron microscopy (SEM), modulated differential scanning calorimetry (MDSC) and analysis of variance for selected mechanical properties. Uncrosslinked CM were used as chitosan patches as one option for timpanoplasty of NZAR. The other options, for comparision purposes were: control group with no perforation, self healing, repair by muscle fascia graft. Histological studies were performed on all TM.

## **Results and Discussion**

Porosity obtained for the CM was 60-70%. There were no significant differences among crosslinked membranes with GDE or uncrosslinked membranes that served as control group. However, when the poroeity of CM crosslinked with GDE compared with CM crosslinked with GA there were significant differences in porosity. Water retention of the CM is generally of 130-190%, being less for the crosslinked CM than for the uncrosslinked CM.

Since chitosan easily absorbs water, for the MDSC tests it was adopted the two scan method to eliminate effects of water in the sample. The first scan shows an endothermic peak, centered at 110 °C which is attributed to moisture absorbed by the CM and to hydrogen bonding among chitosan polymeric chains. It is also observed an endothermic peak centered at 325°C being consistent to degradation reactions. Both peaks disappear during the second scan where it is observed a weak transition at 37°C that could be Tg of the sample already degraded. This value is about the same regardless if CM were crosslinked or not. It is interesting to notice that the crosslinking did not whistand high temperatures during the first scan. When in the modulated mode, separating the signals in reversible and irreversible heats for the first scan allowed the Tg of the CM to be detected due to the high molecular weight and crystallinity of chitosan. These findings are consistent with reported works on CM crosslinked with other agents different from the ones presented in this study[15-17].

The %elongation at break showed statistically significant differences depending upon the type of crosslinker used: GA (16%) or GDE (45-50%). However, among the CM crosslinked with the different GDE, the %elongation at break was proportional to the GDE molecular weight. The Young's modulus for the CM crosslinked with GA presented the highest modulus of all CM (13,000 MPa). It is interesting to notice that there were no statistically significant differences among the modulus of CM uncrosslinked or crosslinked with GDE (1700-2300 MPa). This is probably due to the fact that the GDE crosslinkers give flexibility to the network contrary to the contribution of the GA crosslinker that reduces the range of motions of the polymeric network chains by increasing their rigidity.

#### MACROMEX 2011

NZAR were the model for the test trials of TM repair using chitosan patches. Other techniques such as self healing and fascia graft were used for comparison purposes; the control group was subjected to surgery to expose the TM without further manipulation. Histological images of TM repaired are shown in Figure 1 for the control and the three techniques studied: self healing, fascia graft, chitosan patch. The TM repaired with the chitosan showed an increment in thickness, number of fibroblasts, density of vascularisation, relative to the rest of the TM repaired.



**Figure 1** Histological images of tympanic membranes repaired at 400X. Tissues are in epoxy resin (Durcurpan) and stained with Masson trichromics. (a) control, (b) spontaneous healing, (c) fascia repaired (d) chitosan repaired

#### Conclusions

Crosslinking chitosan with several agents modifies the network structure hence different crosslinking densities are obtained. This leads to an improvement of important parameters in tissue engineering related to mechanical properties and water adsorption such as: tensile strength, elastic modulus and solubility in water. It was found that functionalized polyethylene glycols allowed tailoring the mechanical properties of the CM by increasing the percentage of elongation at break as the size of the functionalized polyethylene glycol was incremented. On the other hand, porosity and water absorption were reduced. These findings agree with the expected behavior for networks where the crosslinking density is reduced by increasing the molecular weight between crosslinking points. Biocompatibility studies showed that the functionalized polyethylene glycols are promising candidates to be used as crosslinkers to obtain biocompatible insoluble chitosan patches. Trial tests have begun for the soluble chitosan patch to repair perforated TM. For tissue engineering applications, it was found that CM show adequate capacity for bio-integration into perforated eardrums in NZAR, and the consequent functional restoration, compared with the traditional muscle fascia.

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# TWO ARMS SEGMENTED COPOLYMERS OF POLY (ETHYLENE GLYCOL AND POLY(ε-CAPROLACTONE)

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#### Abstract

Recently new trends on the synthesis of biodegradable copolymers with drug release functions have been studied. New segmented biocopolymers synthesized from polyethers and polyesters of low molecular weight has been studied. In this work we report the synthesis of segmented copolymers obtained by combining poly(ɛ-caprolactone) (PCL) and poly(ethylene glycol) (PEG) in three stages: (1) synthesis of PCL, (2) synthesis of a prepolymer via end-capping reaction of PEG with toluene diisocyanate (TDI) and (3) synthesis of PCL-PEG segmented copolymer obtained by polycondensation reactions between the prepolymer and PCL. The final product obtained was characterized by Gel Permeation Chromatography (GPC), Fourier Transformed Infrared (FTIR) spectroscopy and Differential Scanning Calorimetry (DSC).

Keywords: Segmented copolymers, GPC, FTIR, DSC.

## Introduction

Segmented copolymers are generally synthesized combining different homopolymers blocks along the main chain<sup>1</sup>. In this regard, the synthesis of the polyurethanes and ether-ester type copolymers has developed since last twentieth century <sup>2,3</sup>. Many of these polymers have been commercialized by their excellent mechanical properties. The synthesis of segmented copolymers includes a wide range of homopolymers as well as biocompatible polymers, which by its biodegradability are subject of increasing interest in biomedical applications <sup>4,5</sup>. PEG is a poly-ether that can be biodegraded by oxidative processes <sup>6</sup>. High rates of biodegradation of PEG can be developed using isolated bacteria in activated sludge <sup>7</sup>. The use of PEG as a component of segmented copolymers has been previously documented in the literature <sup>8,9</sup>. The synthesis of segmented copolymers of segmented and chemical properties of these polymers.

## Experimental

 $\epsilon$ -caprolactone monomer ( $\epsilon$ -CL) with purity of 98%, stannous octanate (SnOct<sub>2</sub>) used as catalyst, 1,6 hexanediol (HD) used as initiator (I), toluene diisocyanate (TDI) and poly (ethylene glycol) molar mass of 1000 g/mol were supplied by Aldrich. Chloroform, petroleum ether and dichloromethane (these solvents with reagent grade) were supplied by Fermont.

## Synthesis of the PCL and derivate copolymers by urethane bondings

The synthesis of PCL was carried out by ring opening polymerization (ROP) technique, as shown in figure 1.



Figure 1. Scheme of the synthesis of PCL homopolymer by ring opening polymerization.

In the first stage were placed 10 mL of monomer in a two-necked reactor of 100 mL immersed in a glycerol bath. SnOct<sub>2</sub> and HD were added to the reactor and allowed to react with constant stirring at a temperature of  $110^{\circ}$ C. The reaction lasted 3 hours. Subsequently, the product was removed from the reactor and allowed to stand for 24 hours to induce solidification of the polymer. The PCL were purified by redissolution in dichloromethane and precipitation with petroleum ether. Table 1 shows the initial compositions of the formulations prepared.

In the second stage, 1 mmol (1 gram) of PEG dissolved in 10 mL of chloroform was placed in a two-necked reactor. This reactor was immersed in a bath of water at 4 °C and kept under constant stirring and nitrogen atmosphere. Then a solution of TDI in chloroform was dropped extending the reaction by two hours. The molar ratio of isocyanate groups of TDI to hydroxyl groups of PEG was 2 to 1 to produce a PEG-TDI prepolymer. Immediately afterwards, in the third stage, the reactor was placed with the product of step 2 in water bath and kept at 60 °C. Then the PCL previously synthesized in the step 1 was added. For the synthesis of the copolymers used a molar ratio of hydroxyl groups of PEG to PCL of 1 to 1 and 1 to 2, respectively. The reaction was carried out again for two hours under a nitrogen atmosphere. The copolymer was purified by precipitation of the product in dichloromethane/petroleum ether. A scheme for the PCL-PEG copolymerization reaction is presented in figures 2 and 3. Table 3 shows the molar ratios used for synthesis the PCL-PEG copolymers.



Table 1. Molar ratio of  $[E-CL[/[I]] and [E-CL]/[SnOct_2]]$  used to synthesize the PCL homopolymer.

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Figure 3. Scheme of the synthesis of PEG-PCL copolymers.

Table 2. Molar ratios of PEG/PCL and TDI used to synthesize the segmented block copolymers of	PCL-
PEG.	

SAMPLE ID	Precursor	PCL/PEG	PEG/TDI
COP1	PCL1	1:1	1:2
COP2	PCL1	2:1	1:2
COP3	PCL2	1:1	1:2
COP4	PCL2	2:1	1:2
COP5	PCL3	1:1	1:2
COP6	PCL3	2:1	1:2
COP7	PCL4	1:1	1:2
COP8	PCL4	2:1	1:2

#### **Results and Discussions**

The results of the GPC for PCL synthesized samples shows a trend of increasing molecular weights when the initiator amount decreases according to the initial formulations employed during the synthesis of the homopolymers (table 1).Table 3 shows the obtained weights for the PCL's synthesized by GPC analysis.

SAMPLE ID	Mn (g/mol)	Mw (g/mol)	Polydispersity
PCL 1	3505	7700	1.75
PCL 2	6121	10405	1.69
PCL 3	7353	10994	1.49
PCL 4	5969	11057	1.85

**Table 3.** Molecular weights and polydispersity index of the PCL's synthesized.

Figure 4 shows monomodal chromatograms of the PCL's synthesized. On the other hand, the FTIR spectra of all the PCL's prepared (not shown) depicts the stretching vibration of the carbonyl group who produces the intense band at 1720 cm<sup>-1</sup>, in the region of 1000-1471 cm<sup>-1</sup> appears to C-O-C functionality near to 2800 cm<sup>-1</sup> can be observed a peak produced by stretching vibration of C-C bond and at 3480 cm<sup>-1</sup> appears a small band due to vibrations of -OH groups.



**Figure 4.** (1) GPC chromatograms of PCL samples (a) PCL1, (b) PCL2, (c) PCL3 and (d) PCL4. (2) DSC thermograms of (A) COP1 copolymer and (B) PCL1.

After carried out the copolymerization reaction of PCL-PEG, the molecular weights were determined by GPC and FTIR technique was used to confirm the success of the synthesis of copolymers. The condensed information of GPC analysis is shown in table 4.

Table 4. Molecular weights and polydispersity index of the PCL-PEG copolymers synthesized.

SAMPLE ID	Mw (g/mol)	Mn (g/mol)	Polydispersity
COP1	54014	29511	1.83
COP2	50235	27836	1.80
COP3	71406	45695	1.56
COP4	71687	43995	1.629

COP5	90133	60275	1.495
COP6	66656	41402	1.609
COP7	91406	58133	1.5723
COP8	92851	58539	1.5861

In a similar manner as observed in the GPC chromatograms of the PCL's, for the PEG-PCL copolymers monomodal chromatograms was obtained as shown in figure 5 (1). The molar weight of PEG-PCL copolymers, determined by GPC, is shown in Table 4. These molecular weights increase respect to the molecular weights of pure PCL. On the other hand, in figure 5 (2) can be appreciate a DSC thermogram of the PEG-PCL copolymers synthesized (COP1 (A) and PCL1 (B)). This themrogram shows that the PEG-PCL copolymers have one glass transition temperature ( $T_g$ ) at -60° corresponding with the PCL homopolymer. This fact suggests that various segments of PEG and PCL are coupled in the skeleton of the copolymer. Similar thermogramas were obstained for all the synthesized samples.



Intensity

**Figure 5.** (1) GPC chromatograms of PCL-PEG segmented copolymers: (a)PCL1, (b) PCL2, (c) PCL3 and (d) PCL4;(2) DSC thermograms of: (A) COP2 and (B) PCL2.



Figure 6. FTIR spectra of: (a) PCL2 and (b) COP2.

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Figure 6 shows the spectra for samples PCL3 and COP8. Similar spectra were collected for the other samples of PCL and COP. The most intense spectral contribution of the PCL spectrum is due to the carbonyl group that appears in 1725 cm<sup>-1</sup>, at lower wavenumbers, in 1190 and 1243 cm<sup>-1</sup> are present a couple bands due to asymmetric and symmetric stretching of C-O-C group. This group is part of the ester group of PCL. On the other hand, at higher wavenumbers in 2866 and 2945 cm<sup>-1</sup>, a doublet is resolved also due to asymmetric and symmetric vibrations, now of the methylene groups of PCL. Finally, in the region from 1300 to 1400 cm<sup>-1</sup> appears a doublet due to vibrations of the terminal OH groups. The spectrum of the copolymer shows distinct differences. In the spectrum of this poly ether-ester, characterized by an intense band at 1116 cm-1 due to asymmetric stretching vibration of the ether group, while in 1062 cm<sup>-1</sup> (weakest) is resolved symmetrical. At higher wavenumbers, at 2883cm<sup>-1</sup> is solved by an intense band of the stretching C-H bond of methylene groups of PEG. In the spectra of PEG-PCL segmented copolymers is evident that co-existence of bands of PEG and PCL. Since the spectra of PCL-PEG were obtained from a purified sample, it may not correspond to a simple mixture of homopolymers.

#### Conclusions

The PEG-PCL copolymers were successfully synthesized; the FTIR and GPC characterization confirms that the coupling of PEG and PCL segments has been achieved. The molecular weight f the PEG-PCL copolymers was higher than the molecular weight of the pure PCL previuosy synthesized. DSC characterization shows that the PEG-PCL copolymers have a only one glass transition temperature near to  $-60^{\circ}$ C.

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# PHYSICAL-EVALUATION OF PROPERTIES OF COMPOSITES WITH HYDROXYAPATITE BIS-GMA

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#### Abstract

By definition a composite is a mixture of different components, in the case of dental composites are a mixture of an organic matrix and fillers inorgánicos. The introduction of the technology of composite resins (composites) in restorative dentistry has been one of the most significant contributions to dentistry in the last twenty years. The advantages of bonded restorations to tooth structure, including conservation of healthy dental tissue, reduced microleakage, postoperative sensitivity prevecion, reinforcement of tooth structure and transmission / distribution of masticatory forces through the adhesive interface of thoot. The polymer matrix based on Bisphenol A-Glycidyl Methacrylate (Bis-GMA), also called Bowen resin has been widely used in recent years as the basis of commercial dental resins, but is limited in its use as a low-grade conversion, a questionable color stability, high viscosity and low resistance to abrasión. The different formulations of resins were characterized in terms of its physical and mechanical properties, assessing stability, fracture toughness, hardness, which allows you to find a formulation that presents the best properties for use in dental resins.

#### Introduction

The composite dental restorations have occurred in the dental society since the 1960s, since then, and after many significant material improvements, the restoration resins still suffer from two key deficiencies: poor mechanical strength and high shrinkage on polymerization. Therefore the research approaches in this area have focused on the evaluation and improvement of materials, combined with the advantages of better esthetic properties. (Sufyan Garoushi, 2011)

The physical, mechanical and esthetic and clinical behavior depend on the structure of the material. Dental composites are basically composed of three chemically different materials: the organic matrix or organic phase, the inorganic binder, filler or disperse phase, and an organosilane or agent of connection between the organic matrix and the filler. The organic matrix of the composite is composed basically of a monomer mono, di or tri-functional, a system of initiation of free radicals (camphorquinone), and stabilizers. The monomer system is considered the backbone of the composite. The Bis-GMA monomer remains the most widely used in the manufacture of current composites. (Garcia & Lozano, 2006) (Figure 1)



Figure 1. Bowen resin (Bis - GMA) - Bis Phenol Glycidyl Methacrylate-(Camps, 2004)

The most significant changes in the composition of the resins have been made with a lot through improvements in landfills. In recent studies, the filler particle size and the amount of it, have proven to be influential factors in determining the physical properties and contraction of the composite. (Sufyan Garoushi, 2011) The problem of dental composites in the restoration is to increase their flexural strength and fracture, thereby extending their useful life in the oral cavity, and also maintain their aesthetic value. (Drummond, 2008)

The degradation potential of the monomer may depend on the chemical stability of the groups present. In the case of dental resins, resistance to oxidative and hydrolytic processes is very important, since the possibility of occurring as a result of exposure to salivary fluids is very doable. Interestingly in commercial practice all monomers of dental restorative resins based on coupling of monomers through ester bonds, which are very susceptible to hydrolysis. (J. P. Santerre, 2001) However, studies of longevity and survival in posterior teeth show that the amalgam has a better record of compounds, which reinforces the need to understand the failure mechanisms of dental composites to improve their survival. Damage to dental composites may be due to the deterioration of the matrix and / or cargo, due to the mechanical strength and environmental burdens, loss of adhesion interfacial microcracks and / or fracture of the filler particles. (Drummond, 2008) In the mouth, the degradation is a complex process, which includes disintegration and dissolution of materials in the saliva, and other physical and chemical degradation such as wear and erosion caused by food, the process of mastication, and bacterial activity. (J. P. Santerre, 2001) (P. J. Koin, 2008)

Most of the materials when subjected to stress and strain for a period of time a fault which is called "fatigue", which is often manifested as fracture, loss of capacity or wear and is influenced by environmental factors. Tension may be static, dynamic or cyclic, and it is hard to imagine how the oral environment acts on the materials used in restoration, as a result of being subject to fatigue, show signs of wear or failure. (Baranl, 2001)

The fracture occurs when the concentration of stress within the material reaches a critical level and is known as fracture toughness. (Drummond, 2008) The fracture mechanics can be used to predict the speed at which a crack can approach a critical size, plus it can be used to determine the conditions under which a crack can be rapid spread. (Drummond, 2008)

A continuous application of mechanical and environmental loads eventually leads to the progressive degradation and crack initiation and growth, resulting in catastrophic failure of dental restorations, this process is influenced by pre-existing holes in the material preparation, imperfect interfaces and residual stresses. (Drummond, 2008)

## Experimental

Mixtures of composite Stuffed / Bis-GMA (womb) Inorganic fillers chosen were hydroxyapatite (HA) synthesized in the laboratory and aluminum silicate (Aldrich), while the resin matrix corresponds to Bisphenol A CAS dimethacrylat Glycerolato 1565-92 -2 Aldrich; polymer dilution as used methyl methacrylate (MMA) and conforquinona as polymerization initiator. The concentrations are shown below:

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Table 2. Composition of samples with 40% Filling / 60% Matrix				
Sample	Identification	Bis – GMA	HA	Aluminium
		%	%	Silicate
				%
1	R40M601	60	20	20
2	R40M602	60	25	15
3	R40M603	60	30	10
	Table 3. Composition	of samples with	45% Filling	/ 55% Matrix
Muestra	Identificación	Bis-GMA	HA	Silicato de
		%	%	Aluminio
				%
4	R45M551	55	25	20
5	R45M552	55	30	15
6	R45M553	55	35	10
	Table 4. Composition	of samples with	50% Filling	/ 50% Matrix
Muestra	Identificación	Bis-GMA	HA	Silicato de
		%	%	Aluminio
				%
7	R50M501	50	25	25
8	R50M502	50	30	20
9	R50M503	50	35	15

Films were prepared additional unfilled

	Table 5. Composition of matrix samples with 100% / 0% Fill					
Muestra	Identificación Bis – GMA HA Silicato d					
		%	%	Aluminio		
				%		
10	R0M100	100	0	0		

With mixtures of the composites were made films that were irradiated for 40 s with a lamp Optilight LD Max (curing light and clareador) No. 4415586008 LD Max 110/240V, 50/60Hz. The samples were characterized by FTIR on a Perkin Elmer Spectrum GX FTIR technique by ATR. Hardness was measured with a Type D Durometer Model 307L Series PTC Instruments 12252 ASTM D2240

#### **Results and Discussion**

The samples were characterized by FTIR (Figures 2, 3, 4, 5). And as you can see in these figures, the band near 3425 cm-1 increases its intensity with increasing concentration of HA, which is a sign of the existence of hydrogen bond type interactions between the filler and the matrix. As if we observe the band of 1715 cm-1 corresponding to the ester groups, which are the type of bonds formed during polymerization of the resin, with intensive, which indicates that the degree of

polymerization is not affected by increasing the amount of the resin matrix, which is a big problem in dental resins, as the degree of monomer conversion is not good, and so they have a low retention of the resin in the teeth. And Figure 5 shows the appearance and increase in intensity of the band of 1027 cm-1 characteristic for HA



With respect to the analysis of hardness, as shown in Figure 7 and Table 6 gives better results for the sample R40M602, which corresponds to a concentration of 25% HA and in general, as reported in the literature, properties of the resin Bis GMA increases with the addition of inorganic fillers, however, contrary to what was reported, by increasing the amount of fillers, the film becomes more fragile, as shown in Figure 6 corresponding to the photographs of the samples, the film with the greatest burden was not possible to obtain fillers, is a mixture of powdery appearance.

		(	/	
	Muestra 1	Muestra 2	Muestra 3	
R40M60	74	82	80	
R45M55	72	73	78	
R50M50	74	70	48	
R0M100				66

Table 6. Results of hardness (Shores) of the sample



#### Conclusions

The hardness of the Bis-GMA resin is increased by adding inorganic fillers, reaching a peak of incorporation of 40% and decreases with increasing filler concentration. The degree of conversion is observed by increasing the intensity of the band of the ester groups is not significant to the concentration of the matrix.

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# SYNTHESIS BY PLASMA OF POLICAPROLACTONE THIN FILMS FOR APPLICATIONS IN CELULAR CULTURE

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#### Abstract

This paper presents the plasma synthesis and physicochemical characterization of a polycaprolactone, PPCL, thin film, used as substrate for the culture of smooth muscle cells, hepatocytes, HepG2, and glial cells. Glass substrates were coated by plasma polymerization with Polycaprolactone at 50 and 100W of power with a synthesis time of 60 minutes. To synthesize the PPCL, the caprolactone monomer was heated at 60°C to vaporize and introduced the vapor in the reaction chamber at a  $3x10^{2}$ Torr pressure, RF 13.56 MHz and 70°C temperature. PPCL films were deposited on glass substrates and were characterized by contact angle, ATR-FTIR, and SEM.

Smooth muscle cells were cultivated on PPCL coated substrates. Primary culture of smooth muscle cells was used to grow starting with of 12.000 cells/cm2 on two substrates of each group (group I 50W, group II 100W) and on a commercial cell culture Petri dish as control. Muscle cells grown in monolayer with febrile characteristics after 48 hours. For each sample, cell counting was performed with a Neubauer chamber and followed a protocol of MTT to quantify cell viability. The cellular culture in vitro of hepatocytes, HepG2, and glioma cells were also performed. The results indicate that thin films of PPCL are conducive to culture cells of the three types, they are anchored, reproduce and remain functional.

#### Introduction

The e-Polycaprolactone (PCL) is a resorbable and semi-crystalline polyester and is biodegraded by hydrolysis. The degradation products are metabolized and secreted by the human body, so that the PCL is a material widely used in medical applications. Because of relatively long degradation time, has been used for implants in vivo, such as reasorbable sutures, tissue engineering, as a means for controlled release of drugs and bone graft substitute [1]. There are different methods to polymerize the PCL, chemical, electrochemical, electrospinning, and plasma polymerization. The plasma polymerization is a process that allows that a monomer is deposited as a thin film on any substrate. The plasma polymerization is the formation of polymeric materials under the influence of a partially ionized gas (plasma). The polymer is formed by introducing into a vacuum reaction chamber, the reactants in a gaseous state and ionized by the influence of an electromagnetic field generated by the difference in potential between two metalic electrodes. These ionized particles, interacting with the surface of a material, coated changing their surface properties or by depositing a thin film [2].

The objective of this work is exploring the possibility of coating substrates with plasmasynthesized PCL, so as to produce a surface that is useful for applications in tissue engineering. For this, cultured smooth muscle cells on a Petri dish as a control, the material normally used for cell cultures and two different samples of PCL synthesized by plasma. The cytotoxicity of the PCL thin films has studied, and the cell proliferation where the cells maintain their natural morphology.

## Experimental

#### Primary culture of cells smooth muscle.

For this work, primary culture of smooth muscle cells obtained from a biopsy of muscle tissue of the vagina is used, made in 2008 by Dra. Atlántida Raya at the Hospital Infantil de México "Federico Gómez". The vaginal tissue removed was cut with a scalpel to obtain pieces of about 1 mm2 and placed in a Petri dish with 10 ml of culture medium modified DMEM (Dubelcco's Modified Eagle Medium, Gibco) for a disgregation by enzyme by adding Collagen Type II with a concentration of 200 IU/ml and incubate for 24 hours at 37 ° C. The cells obtained were seeded in culture dishes with 10 mL of DMEM culture medium, previously supplemented with 10% fetal bovine serum, 100 IU / ml penicillin, 100  $\mu$ g/ml streptomycin and 100 IU / ml of antifungal (all reagents GIBCO), to enrich their nutrients and avoid any contamination in the crop. Cells were maintained at 37 ° C in an incubator with an atmosphere of 5% CO2, to observe the confluence of cells forming a monolayer, indicating the time of subculturing cell proliferation as a technique to obtain a greater number of cells.

#### Synthesis of PCL thin film

For the PCL plasma polymerization on glass substrates a glass tubular reactor of 9cm external diameter and a length of 25cm was used, see Fig. 1. The reactor is connected to a radio source Dressler, CESAR 1500 RF at 13.5MHz, and a vacuum system. To carry out the polymerization reaction of caprolactone monomer was heated to  $60 \degree C$  to vaporize and driver the monomer vapor to the reaction chamber at a pressure of 2.5x10-1 Torr. Were prepared 2 different types of substrate to power of 50 and 100 W, both with a synthesis time of 60 minutes.

## Culture cell on glass substrates cover with PCL

Batch of frozen cells is took from the cryotube and thawed by shaking at  $37 \degree C$ , this operation takes less than 1 min. After the contents were placed in a Petri dish and culture medium was added at  $37 \degree C$  at a leisurely pace to complete 10 mL, samples were incubated at  $37 \degree C$  and 5% CO2. After 24 hr, there was change of culture medium to remove DMSO, which is cytotoxic at room temperature. Cells were maintained in culture until confluence to have the desired number of cells for the experimentation.

Cell count was performed using the Trypan blue reagent and plated 12.000 cells/cm2 in each of the experimental samples. We used a control (Petri dish), 2 PCL substrate samples obtained PCL plasma at 50W and 100W.

## Proliferation and cytotoxicity assay

After 48 hr of culture, cells were trypsinized to perform a cell count and quantify cell concentration present on each test substrate. In the case of PCL substrates, spent each to a sterile Petri dish and 4 mL of trypsin applied after first washing the cells and remove the culture medium present, then repeated the maneuver to incubate cells for 5 min at 37 ° C and allow the take of a sample and suspended. After this time, trypsin was removed and cells resuspended in fresh culture medium, dividing each cell solution in 2 containers. To quantify the cell count and proliferation, was diluted with 20  $\mu$ L of each cell solution was diluted with 20  $\mu$ L of Trypan Blue, and then do a count of living cells by light microscopy using a Neubauer chamber. To study the cytotoxicity of each substrate, we performed MTT assay is a colorimetric assay to measure mitochondrial activity as cells metabolize MTT reagent, which is purple color. For this, 1 mL of each cell solution was taken and centrifuged for 10 min at 2000 rpm to discard the

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supernatant. Cells were resuspended in 1 mL of culture medium (without serum to avoid interference in the experiment) and added 200  $\mu$ L of MTT reagent and then incubated for 4 hr at 37 ° C. Isopropanol was then added to solubilize the formazan crystals and measuring the absorbance of the samples in duplicate by placing 30  $\mu$ L of each sample into the well of the ELISA plates, using an ELISA plate reader Geniuses at a wavelength of 595nm.



Fig. 3 PCL SEM.

# **Results and Discussion**

# **FTIR-ATR Analysis**

Figure 2 shows the infrared spectrum in mode attenuated total reflectance of the PCL, the spectrum shows broad bands and complex characteristics of the polymers synthesized by plasma technique. The vibration corresponding to the OH groups is observed at  $3350 \text{ cm}^{-1}$ . The vibration in 2923 cm<sup>-1</sup> corresponds to the asymmetric vibration of methyl aliphatic -CH<sub>2</sub>, while the symmetrical vibration of the same group appears in 2859 cm<sup>-1</sup>. 1741 cm<sup>-1</sup> appears in a strong and sharp band due to stretching vibrations of carbonyl group C = O. The band centred in 1190 cm<sup>-1</sup> is result from the stretching vibration of CO-O bond, at 730 cm<sup>-1</sup> a small band attributed to bending vibrations of the groups - (-CH2)<sub>n</sub> with n> 4.

As the PCL is semicrystalline polymer in the solid state, the infrared spectrum shows the contributions of both the crystalline and amorphous phase. Stretching vibrations of the carbonyl group associated with the crystalline phase can be observed in 1741 cm<sup>-1</sup>. The vibrations of the carbonyl group associated with the amorphous phase can be seen in 1736cm<sup>-1</sup>. Also the band at

1284cm<sup>-1</sup> is associated to the crystalline phase of PCL.

## Analysis SEM

The scanning electron microscopy of PCL deposited by plasma polymerization is show in Fig 3. 3 (a) it was taken at a magnification of 250X and shows a smooth polymer film with pieces scattered over. By taking an approach (3b, 10000x) a rough surface like a carpet surface is shown, this type of rough surface can allow that different types of cells are anchored to this surface.

Table 1. Calculating the value of absorbance at 595 nm of formazan metabolized by 60,000 cells from each sample.

Sample	Cell/mL	Absorbance 595 nm,	at	Absorbance calculate mitochondrial activiti of 60,000 cells *
Control	230,000	1.3394		0.28035
100W A	85,000	0.7241		0.44205
100W B	60,000	0.8818		0.81275
50W A	110,000	0.7802		0.35645
50W B	70,000	0.9876		0.77735

## **Culture Cell**

Fig 4 shows photographs of cell cultures on each type of test substrate. It can be see how after 48 hours of culture, all the substrates have numerous cells that present their characteristic morphology with spindle-shaped cells. When performing the cell count, the control has a cell concentration of 23,000 cells/cm2 in PCL synthesized to 100W have 22.666 cells/cm2 in the control and have 29.333 cells/cm2 in PCL of 50W, therefore, there is cell proliferation between 33 and 144% of the substrates with PCL and 92% for the control, without having a clear significant difference between them. In the cytotoxicity test, is calculated the absorbance is calculated for the case of measuring mitochondrial metabolism of MTT to formazan in 60,000 cells from each experimental sample (see Table 1).



Fig 4. Photographs of muscle cell culture: a) Petri dish, B) PCL substrate synthesized by plasma 50W (right side, left side Petri dish), C) PCL substrate synthesized by plasma 100W (right side, left Petri dish). Obtained using optical microscope with 10x magnification.

#### Cellular culture of hepatocytes and neuroblastoma-cells

Fig 5 shows the cell growth of hepatocytes (a) and rat neuroblastoma cells (b). As can be seen in the two substrates coated with PCL the cells grow, proliferate and develop. (a) shows the classic growth of HEp-G2, has a polygonal morphology and spread almost all over the substrate to form a monolayer. In (b) it can be seen that the cells are developing axons and even touch each other through the axons, they have the characteristic morphology of these cells and also tend to form a monolayer.



Fig. 5 In (a) is shows the hepatocyte cell culture, Hep-G2, In (b) is show the cultivation of mouse neuroblastoma cells N1E115.

#### Conclusions

Plasma modification with PCL shows a good cell culture surface, this was probed with tree different kind of cells showing excellent behavior as compared with culture petri dishes, plasma modification may be apply to Tissue Engineering scaffolds and take advantage of the cell adhesion.

#### Acknowledgements

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## EFFECT OF GLYCEROL ON THE PROPERTIES OF POLYVINYL ALCOHOL-AGAR BIODEGRADABLE FILMS

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Polyvinyl alcohol-agar films are flexible, transparent and biodegradable materials based on synthetic and biopolymer sources, these films prepared by solution cast method can be used in food packaging, drug delivery and other applications [1]. The addition of glycerol (GLY) as a plasticizer, can modify several functional and physico-chemical properties of these films, such as increasing flexibility and extensibility, moisture sensitivity, etc. [2,3].

Biodegradable films of poly(vinyl alcohol) (PVOH) and agar blends have been prepared by solution casting method using glycerol (GLY) as plasticizer. Both neat PVOH and agar films are transparent. However, their blends and GLY addition produced a slight opacity in films due to phase separation. As the amount of agar is increased in the film, it leads to a decrease of the tensile strength and reduces the elongation at break. At 75% wt of agar a significant improvement on the mechanical properties is observed. The films produced were also characterized by FTIR spectroscopy, thermal analysis (differential scanning calorimetry DSC and thermogravimetric analysis TGA), x-ray diffraction (XRD) and scanning electron microscopy. As GLY is incorporated into the PVOH-agar network resulted in a reduction of intermolecular interactions and proximity of PVOH and agar chains, and the increase of mobility of polymer chains.

In conclusion, PVOH-agar films have been improved by the addition of GLY. It widened the applications of this system in food packaging as expected.

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Cardiac infarction is one of the leading causes of death in the México and the US [1, 2]. Many of the problems derived from this are due to wall thinning, cardiomyocytes loss and lack of contractility. Our approach is to seed Cardiac Progenitor Cells (CPCs) into a scaffold so they can differentiate in vitro before implantation. This cardiac patch would serve as an in situ reinforcement and promote vascular integration and cell repopulation. The objectives of this work were to synthesize poly(urethane-urea) (PUUs) polymers from PCL2000, HMDI and BDA with different hard segment (HS) contents [3], characterize them, prove biocompatibility by seeding them with Sca-1+/CD45- (CPCs), and, obtain scaffolds by a solvent casting/porogen leaching technique combined with centrifugation to enhance pore connectivity.

The work presented includes the analysis of the materials by FTIR and NMR to corroborate the synthesis results, DSC and DMA studies to determine the thermal properties of the polyurethane ureas and the influence of the hard segment content in them. The next step was to expose these materials to the CPCs to determine biocompatibility. Bright field microscopy and CyQuant studies were used to determine the morphology and proliferation of cells respectively. The last part will present the fabrication of scaffolds made from this PUUs and the SEM imaging to observe the pore sizes and characteristics.

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# PLASMA SURFACE MODIFICATION OF BARIUM SULFATE POWDER USED IN BONE CEMENT FORMULATIONS

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#### Abstract

Plasma technology is widely used to alter the surface properties of materials without affecting their bulk properties. The treated materials have found various applications in automobiles, microelectronics, biomedical and chemical industries. Specific surface properties like hydrophobicity, chemical structures, roughness, conductivity, etc. can be modified to meet the specific requirements of these applications. Development of new biomaterials typically takes a long time due to extensive tests and lengthy approval procedures. Plasma surface modification offers an exciting alternative by modifying selectively the surface while preserving the mechanical and biological properties of conventional biomaterials to suit particular needs.

A very important element in the bone cement formulations is the radiopaque agent used, which is essential for the bone cement to be radiologically detectable; however, the addition of this inorganic compound within the PMMA matrix produces that the mechanical strength of cement decreases due to the incompatibility between them. In this work, barium sulfate powder was modified by plasma polymerization using methyl methacrylate monomer (MMA). The surface modification of barium sufate was performed as follow: powder was first treated with atmospheric plasma for 15 minutes at 15 W before the vapor of MMA monomer was introduced into the reactor chamber at the same plasma power level for 5 hours. The modified particles were characterized by water contact angle, Fourier Transform Infrared Spectroscopy (FT-IR), thermogravimetric analysis (TGA) and Scanning Electron Microscopy (SEM). It was observed that the water contact angle of the modified barium sulfate particles become slight hydrophobic ( $21^{\circ} + 4$ ) compared to the unmodified particles which were totally hydrophilic. FTIR analysis of modified particles revealed the presence of a carbonyl band at 1724 cm<sup>-1</sup>. Both results confirm the deposition of PMMA onto barium sufate surface. TGA analysis shows a 0.6 % of mass weight loss, which can be associated to the degradation of deposited PMMA. Finally, bone cements were prepared and characterized; it was observed that the tensile strength of cements increases from 26 MPa for cements prepared with unmodified particles to 32 MPa for those formulations prepared with modified particles.

#### Introduction

Radiopacity is a desirable property in bone cement formulations used in surgery as it allows postoperative assessment of the fate of the implant using X-radiography. The bone cement itself is not radiopaque, as it is mainly composed of elements such as carbon, hydrogen and oxygen, which have a low electronic density; therefore, this property is achieved by incorporating the inorganic materials like barium sulfate or zirconium oxide [1-2]. However, it is well know that these agents do not mix well with the polymeric matrix due to thermodynamic reasons, leading to a decrease in mechanical properties of cements [1,3-5].

Several authors have suggested that a promising alternative for achieving radiopacity in bone cements formulations consists in the chemical modification of polymers by introducing bromine or iodine to methacrylate monomers. The polymerization or copolymerization of such monomers would produce X-ray opaque materials without the disadvantages of two-phase systems. Thus, various monomers containing iodine or bismuth [6-9] have been synthesized and copolymerized giving rise to radiopaque materials to be tested for application in the medical field; however, these materials have not been still approved by FDA.

On the other hand, plasma technology is widely used to alter the surface properties of materials without affecting their bulk properties. This technique also offers an exciting alternative by modifying selectively the surface while preserving the mechanical and biological properties of conventional biomaterials to suit particular needs.

With this in mind, the aim of this work was modify barium sulfate powder (approved by FDA for use in bone cement formulation) by plasma polymerization using methyl methacrylate monomer (MMA) in order to enhance the compatibility between the polymeric and inorganic phases of the bone cement formulations and therefore, the mechanical properties of these materials.

## Experimental

## Plasma Surface Treatment

Barium sulfate was purchased from Aldrich Chemical Co. (reagent plus 99%) and it was used as received. The surface modification of barium sulfate was performed as follow: powder was first treated with air plasma for 15 minutes at 15 W, 13.59 MHz RF and  $2.5 \times 10^{-1}$  Torr, before the vapor of MMA monomer was introduced into the reactor chamber at the same plasma power level for 5 hours.

## Fourier Transform Infrared Spectroscopy (FTIR)

Infrared spectra of the barium sulfate samples were obtained by Diffuse Reflectance technique (DRIFT) at room temperature using a Nicolet Magna Spectrometer with a resolution of  $4 \text{ cm}^{-1}$  averaging 100 scans in the 4000–400 cm<sup>-1</sup> wavenumber range.

#### Thermogravimetric Analysis

Thermogravimetric data were collected from 50 to 600°C at 10°C/min under dry nitrogen atmosphere by using a Perkin Elmer TGA-7; sample masses ca. 10 mg were used.

## Water Contact Angle

The effect of plasma treatment on the surface properties of barium sulfate samples was evaluated through water contact angle measurements using the sessile drop technique. A distilled water droplet was deposited onto BaSO<sub>4</sub> pellets in a Tantec Cam-Plus-Micro system.

## **Scanning Electron Microscopy**

Morphology was observed by SEM using a Jeol 6360 LV. Samples were gold coated and observed using an accelerating voltage of 20 kV. EDX was also empoyed in order to determine the chemical composition of barium sulfate surface.

#### **Preparation of bone cements**

The experimental bone cements were formulated by adding the liquid component to the solid (powder) component at room temperature (25°C). The powder component consisted of Nictone (PMMA) beads, benzoyl peroxide (BPO) and barium sulfate (non-treated and plasma treated) while the liquid component consisted of MMA and dimethyl-p-toluidine. BPO and BaSO<sub>4</sub> were added to the solid phase at 1 and 10 % w/w, respectively. A weight ratio of powder to liquid of 2 was kept in all cases and the cements were prepared by hand mixing without vacuum.

#### Characterization of bone cements

Compression tests of acrylic bone cements were conducted according to the ASTM F451 while

the tensile tests were carried out according to the ASTM-D638. The compression tests were performed on cylindrical specimens (6mm diameter, 12mm height) at a cross-head speed of 20 mm/min whereas tensile tests were conducted on specimens type IV at a cross-head speed of 5 mm/min.; the maximum strength and elastic modulus for both tests were recorded.

#### **Results and Discussion**

Figure 1 shows the FTIR spectra of the barium sulfate particles. As noted, the spectrum of nontreated particles showed absorption bands at 3414 and 1631 cm<sup>-1</sup> which are associated to stretching and bending vibrations of adsorbed water molecules. Bands at 1200 and 1108 cm<sup>-1</sup> are related to symmetrical vibration of  $SO_4^{2-}$  and the peak at 622 cm<sup>-1</sup> is due to the out-of plane bending vibration of the  $SO_4^{2-}$  [10-11]. It was also observed that the spectrum of barium sulfate treated with PMMA plasma was very similar to that non-treated one, although subtle differences were observed as the appearance of the carbonyl band at 1724 cm<sup>-1</sup> (see Figure 1b), which is typical of stretching vibration of ester group of PMMA. The presence of last band confirms the surface modification of barium sulfate particles. The peaks appeared at around 2000 cm<sup>-1</sup> are overtones and combination bands of the sulphur-oxygen stretching and bending vibrations; these peaks do not affect the identification of the substance involved in the experiment [10,12].



Figure 1. FTIR spectra of barium sulfate particles.

Table 1 shows the chemical composition of barium sulfate particles obtained from EDX analysis. As expected, particles are composed mainly of barium, sulfur and oxygen; although those particles treated with PMMA plasma also exhibited carbon. Variations of chemical composition are due to that analysis was performed on particles surface.

Table 1. Chemical of	composition o	of barium	sulfate particles.
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Element	Non-treated	Plasma Treated
	(%w)	(%w)
Ba	82.50	47.74
S	13.24	11.54
0	4.26	33.36
С	-	7.35

Figure 2 shows the water contact angle formed onto surface of barium sulfate pellets. It can be seen that particles treated with PMMA plasma exhibited a higher water contact angles (21°) than non-treated; this indicates that particle surface became more hydrophobic like PMMA.



Figure 2. Water contact angle for barium sulfate particles (a) non-treated and (b) plasma-treated.

On the other hand, Figure 3 shows that particles treated with PMMA plasma exhibited a slightly higher mass loss (ca. 0.6 wt%) than observed for non-treated particles, which can be assigned to the degradation of PMMA deposited onto surface of particles.



Figure 3. TGA of barium sulfate particles.

Results of the mechanical properties of cements prepared either non-treated and plasma treated barium sulfate are shown in Table 2. As observed, cements prepared with plasma-treated barium sulfate particles exhibited higher strengths and moduli than that prepared with non-treated particles. This indicates that surface modification carried out onto barium sulfate particles increase the adhesion between radiopaque agent and polymeric matrix.

Table 2. Mechanical properties of cements prepared with barium sulfate particles.

Sample	Tensile test	test Compressive Test		
	Strength (MPa)	Modulus (GPa)	Strength (MPa)	Modulus (GPa)
Non-treated	$41.33 \pm 1.40$	$2.67\pm0.02$	$97.75 \pm 1.78$	$1.71\pm0.06$
Plasma Treated	$45.83\pm0.73$	$2.76\pm0.01$	$103.64\pm0.65$	$1.97{\pm}0.03$

## Conclusions

Barium sulfate powder was modified by plasma polymerization using methyl methacrylate monomer (MMA). Surface modification of radiopaque agent was corroborated by FTIR, SEM-EDX, TGA and water contact angle. Plasma modification leds to cements with enhanced mechanical properties.

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#### PLASMA POLYPYRROLE COATINGS ON METALLIC SUBSTRATES IN CONTACT WITH BLOOD-LIKE PHOSPHATE SOLUTIONS

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Polymeric coatings in human metallic implants are applied to avoid direct contact of metallic surfaces with tissues and to stimulate cell growth on the implant. Polypyrrole (PPy) is studied in this function because of its biocompatibility. In this work, self-expanding models of Stents made of stainless steel and nitinol (Ni-Ti) were coated by plasma with PPy to study their permanence on the surface in contact with phosphate buffered saline solutions (PBS) of pH similar to blood. The concentration of PBS was NaCl: 24 mmol/L, Na2HPO4: 10 mmol/L and KH2PO4: 3 mmol/L. The immersion time of coated samples was studied up to 336 hrs. Optical microscopy showed high resistance of coatings to solutions in the first hours and swelling of polymers after that with small segments of separation between polymer and metal. The contact angle of PPy on flat surfaces and PBS solutions (30°-60°) is also discussed.

## PLASMA POLYPYRROLES WITH GAMMA IRRADIATION

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This work presents a comparison of structural, morphological and electrical properties in plasma polypyrroles (PPy) using monomers sensitized with gamma irradiation in doses of 18 and 40 KGy. Depending on the dose, gamma irradiation produces chemical bond breakage and is applied in this work to create free radicals in monomers before the polymerization to increase networking during the polymerization.

After gamma irradiation, the monomers were polymerized by low-pressure, rf, resistive, electrical glow discharges. The polymers were obtained as thin films adhered on the reactor's walls. The results indicated that gamma irradiation reduces multiple bonds in PPy due to the formation of new bonds in the structure. Another result is that polymers obtained with gamma sensitized monomers ( $\gamma$ PPy) do not easily accept iodine doping as PPy does. The surface of non-irradiated PPy is rough formed by compacted layers. However in  $\gamma$ PPy roughness increases showing a bigger number and size of pores. On the other hand, polypyrroles irradiated after the synthesis (PPy $\gamma$ ) present lifting of layers. This effect does not appear in  $\gamma$ PPy.

## ELECTRICAL CONDUCTIVITY OF PLASMA POLYPYRROLE IN CONTACT WITH HUMAN-LIKE IONIC SOLUTIONS

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This work presents a study about the conductivity of plasma polypyrrole (PPy) in contact with solutions of salt concentration similar to human tissues. PPy is a conjugated biocompatible polymer in which the electronic distribution produces partial relocation forming radical cations on segments of polymer in contact with different compounds. PPy particles with different sizes are being studied as implants in central nervous system to restore lost neuronal communication after severe injuries. If the connections between nerve cells do not work appropriately the consequences may be, among others, total or partial immobilization of the body. Particle size, hydrophilicity and conductivity of polymers are essential in the reconnection. The study discusses particles of different sizes in the range of neuronal nuclei and solutions with different concentrations of salts, particularly with sodium and potassium ions which are mainly used in the ionic transfer in neuronal membranes. Plasma PPy was synthesized as films using low-pressure, rf, resistive, electrical glow discharges.

The films were mechanically ground up to obtain microparticles. The electrical conductivity was studied in this condition with the addition of human-like ionic solutions.

#### STRUCTURE OF PYRROLE-ETHYLENEGLYCOL PLASMA COPOLYMERS

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A study about the structure of copolymers based in random combinations of etylenglycol, pyrrole and iodine synthesized by plasma is presented in this work. These oxygenated-nitrogenated hydrophilic copolymers capable of transfering electrical charges can be used as implants in the central nervous system. The copolymers were synthesized with resistive rf glow discharges in a 1500 cm<sup>3</sup> tubular glass reactor at 10<sup>-1</sup> mbar and 40-100 W. The polymerizations occurred in gas-phase, in which the monomers combined within the reactor to produce random copolymers.

The structure of copolymers has C=C, C=N, C=O, C=N, C-O and C-I functional groups. Multiple bonds, not belonging to the initial reagents, were generated by the dehydrogenation of monomers and intermediate compounds during the polymerization; these bonds have been found in many plasma polymers. Alternated bonds of different electronic density facilitate the movement of electrical charges in polymers. The electronic conductivity was measured as a function of temperature between 15 and 100°C and it was in the interval from  $10^{-9}$  to  $10^{-4}$  S/m. The activation energy was calculated with the Arrhenius model, obtaining values from 0.36 to 1.1 eV. It is discussed the main atomic chemical states in the copolymers.
#### MACROMEX 2011

#### SYNTHESIS OF POLYFURAN BY PLASMA

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Furan, pyrrole and thiophene are the most common heterocycles of 5 members. The last two monomers have been used in polymer research dedicated to biological and photoactive applications, respectively, pyrrole for its nitrogenated and thiophene for its sulfured compounds. However, the oxygenated heterocycle, furan, has escaped these tendencies. This work presents a study about the synthesis of polyfuran by plasma with the purpose of studying its structural, electric and morphological properties. The syntheses were carried out with low-pressure, resistive, electrical glow discharges exploring the possibility of obtaining polyfuran (PFu) in powder and film. The results indicated that the polymers have structure with functional groups as C-O and C=C from the monomer and C=O and O-H from the recombination of radicals and dehydrogenation during the polymerization. The powder contains spherical particles with average diameter between 70 and 850 nm. The polymers have contact angles as a function of the energy applied to the synthesis obtaining hydrophilic films with angles from  $43^{\circ}$  to  $90^{\circ}$  and hydrophobic films from  $90^{\circ}$  to  $108^{\circ}$ . Conductivity of the materials was calculated in the  $10^{-6}$ - $10^{-9}$  S/m interval with activation energy from 2.87 to 2.86 eV, which locates this polymer in the insulating organic polymers.

## FABRICATION AND BIOLOGIAL CHARACTERIZATION OF COMPOSITEOF POLYLACTIC ACID -HIDROXYAPATITE COATED WITH POLYPYRROLE FOR USE AS SCAFFOLDS IN BONE TISSUE

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#### Abstract

This work presents the fabrication of porous matrices of polylactic acid (PLA) and hydroxyapatite (HA) coated whit polymer of pyrrole synthetized by plasma. The composite was made first by electrospinning nanometric and micrometric fibers of PLA-HA from solutions at different concentrations and conditions of the spinner. The resulting porous materials are coated by plasma polymerization of pyrrole (PPy) due to its good results in cell adherence, composites were characterized by optical microscopy and SEM.

#### Introduction

Usually a graft or bone substitute is required to help repair a skeletal deficiency due to some trauma or some sort of disease like osteosarcoma [1,2]. Tissue Engineering is an alternative to generate synthetic bone preservation in providing patient progress, functional recovery and mobilization. The biomaterials that can be used as bone substitutes should possess biocompatibility which is intimately linked to their surface properties, these polymeric materials can be found combined with ceramic materials that are better in replacing bone tissue [3]. Polylactic acid is a polymer, which has biodegradability and biocompatibility. Hydroxyapatite (HA) is a ceramic, which is the largest inorganic part of bone, and is biocompatible and resilliant. [4].

Electrospinning technique is used to manufacture of porous matrices, it consist in the application of a voltage ranging from 10KV up to 30KV to create a strong electric field seeking to attract electrically charged particles of a polymer solution from a nozzle into an area where it solidifies (collector) to form microfibers and nanofibers [5]. In this paper we use the plasma polymerization technique to synthesize films of Polymer of pyrrole (PPy) and modify the surface properties of PLA-HA matrices [6]. Using PPy is an advantage in the proliferation of bone-forming cells (osteoblasts) due to its electrical conductivity and cell stimulation [7]. The samples were characterized by optical microscopy and scanning electron microscopy (SEM).

To test the PLA and HA matrices coated with PPy, it is suggested that in vitro culture be used, for which a bone biopsy is performed, a culture of bone cells (osteocytes, osteoblasts and osteoclasts) is produced, sequential seeding of these cells and arrays for the newly formed tissue are made, which is to evaluate the microstructure and pre-feasibility studies. [8].

#### Experimental

#### **Preparation of the solution**

Briefly, you have 10 ml of solvent, 90% chloroform (9 ml) and 10% ethanol (1 ml). After PLA

Sample		Solids		Volume		Valtara
	PLA(g)	HA(g)	(g/ml)	(ml)	%HA	(KV)
M1	1.2	0	0.12	40	0	30
M2	1.2	0.3	0.15	10	25	30
M3	1.8	0.3	0.21	10	16	30
M4	1.2	0.3	0.15	20	25	30
M5	1.2	0.1	0.13	20	8.3	30
M6	1.8	0.1	0.19	30	5.5	30
M7	1.8	0.3	0.21	40	16	30
M8	1.8	0.2	0.20	80	11	30

and HA was added in different amounts for each array as shown in the table 1. This solution was allowed to dissolve for 5 hours at room temperature until it is homogeneous.

### **Film preparation**

The electrospinning system is presented schematically in Figure 1. It consists of an injection mechanism in which the polymer solution is deposited PLA and HA. This solution travels from the positive electrode (the needle) to the collection electrode which is a rotating drum 7 cm long and 5 cm in diameter that is earthed; the distance between electrodes is 10 cm. When the solution is solidified fibers form a matrix with nano and micrometric varying lengths. The voltage applied to this type of solution is of 25KV to 30KV. It is noteworthy that the diameter of the needle is chosen depending on the amount of HA in the solution.



Figure 1. Schematic illustration of Electrospinning System

The matrices obtained are removed from the manifold, placed in a petri dish and kept until the time of analysis, as shown in Figure 2:



Figure 2. Schematic illustration of synthesis of a matrix of PLA-HA

Second US-Mexico Meeting "Advanced Polymer Science" and XXIV SPM National Congress Riviera Maya, Q. Roo, México. December 2011 In this paper we use the plasma polymerization technique to synthesize polypyrrole films and thus modify the surface of the PLA and HA matrices in order to facilitate the adhesion of bone cells and that the polypyrrole is a stimulator of cell growth and has good electrical conductivity. The plasma polymerization reactor consists of a glass tube (Pyrex), length 25 cm, 9 cm in outer diameter and wall thickness of 0.7 cm. At each end of the tube is placed a stainless steel lid with two outputs. The covers have a hole in the middle to insert a stainless steel electrode, which consists of a circular rod and a flat circular plate of 6 cm. During polymerization, the separation between the electrodes was approximately 10 cm. [9].

Pyrrole was used (Sigma-Aldrich). Arrays of PLA-HA, were placed in the center of the reactor. Before starting the polymerization, the reactor was purged for ten minutes to remove impurities. Then pyrrole was introduced to cover these matrices. The conditions at the beginning of the polymerization were: 1.2x10-1 Torr, 14 W and 13.5 MHz.

#### **Results and Discussion**

Samples analyzed by light microscopy at 200 magnification, are shown in Figure 3; they are taken as representative samples, M3, M6 and M8 which present Hydroxyapatite aggregates. M1 is different in containing only PLA. It also shows that with the greater the amount of solution injected, the morphology of the matrix is effectively closed, by forming fibers of different diameters.





M6 HA 5.5%, 30ml solution injected



M3 HA 16%, 10ml solution injected



M8 HA 11%, 80ml solution injected

Figure 3. Optical microscopy of arrays with different concentrations of HA

Analysis was also performed by SEM, we used the scanning electron microscope field emission JEOL JSM 7600F. Arrays were analyzed at different magnifications as shown in Figure 4 and again M1 without HA has a homogeneous morphology, unlike the M3 for example, which shows "rough" morphologies due to aggregates HA.

Scanning electron microscope field emission



Figure 4. Schematic illustration of SEM of M1 and M3

Figure 5 shows these peculiar morphologies due to the presence of HA in the matrix's composition; either with less solution injected like M5 or those that are more like M8 with 80ml of solution injected. Furthermore, the matrices are not necessarily better if they have more hidroxyapatite but more fibers, then you can combine PLA-HA concentrations as M2 or M3 and inject as much solution as you need to obtain a matrix rich of HA and fibers. The diameters of the fibers in the matrices have sizes between 800 nm and approximately 10µm, and they have pores large enough to allow movement of osteoblasts in these matrices.



M8 HA 11%, 10 ml solution injected (500x 10μm, 1000x 10μm, 4000x 1μm) Figure 5. Schematic illustration of SEM of M5 and M8

#### Conclusions

It was confirmed that the technique of electrospinning produces porous matrices and gave good results by injecting solution of PLA-HA, matrices were obtained with pore size of micrometers to be acceptable for the proliferation of osteoblasts. We were able to combine the properties of polylactic acid with the hydroxyapatite, obtaining resistant but not brittle matrices. What remains is the biocompatibility test for which it is suggested that these matrices are used for growing bone cells in vitro seeking adhesion and cell proliferation, If successful, we would be talking about a good base to produce a biomaterial that offers an alternative for bone tissue repair.

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## POLY(ASPARTIC ACID) PRECURSOR OBTAINING BY REACTIVE EXTRUSION

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In recent years there has been increased interest in biodegradable particularly biodegradable polymers. Green chemistry seeks to reduce environmental damage caused by chemicals and processes[1]. In chemical industry, green polymers should be produced at a low cost. The biotechnological production of L-aspartic acid has been recently carried out on an industrial scale and economically feasible [2,3]. Thermal polycondensation of aspartic acid occurs readily poly(aspartic acid) so that great potential to solve environmental problems [4,5].

In this work a novel method in the biodegradable polymer obtaining is described: the reactive extrusion of amino acids. In a first stage, it was focused in the formation of the polysuccinimide (poly(aspatic acid) precursor), using a single-srew extruder. The temperature profile and the time of residence were stablished. The polysuccinimide samples thus obtained were analyzed by FTIR and DSC.

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## SCAFFOLDS ELECTROSPINNING OF POLYVINYL ALCOHOL AS DRUG DELIVERY SYSTEM.

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#### Abstract

This paper seeks to incorporate ascorbic acid, AA, within a polymer scaffold composed of nano and micro fibers of polyvinyl alcohol, PVA. Scaffolds of PVA and PVA/AA were made through the electrospinning technique, 1g of PVA was dissolved in 10ml of distilled water, PVA-0.1 g/ml, and in 10ml of distilled water was dissolved 1g of PVA and 3.3g of AA. SEM and optical microscopy were use to studied the samples. PVA shows a network structure composed of fibers of different diameters with a pore size of about 10µm while for the PVA/AA, SEM shows the formation of a film on the fibers, possibly due to the presence of AA. Samples of PVA/AA were immersed in distilled water to study the rate of release of ascorbic acid.

#### Introduction

The need to employ drug transport systems with high specificity and activity at the site of application, without toxic effects through the use of polymeric materials as drugs carriers to regulate and dispense specific applications [1]. Polyvinyl alcohol (PVA) takes the role of polymeric support as it is hydrophilic, nontoxic, biocompatible, with good mechanical properties and very stable for long periods in different conditions of temperature and pH [2], and the dosing agent is ascorbic acid which has an accelerating effect on the healing process, prevent allergies, acts as a coenzyme in the synthesis of collagen and intercellular cementing substance in the blood capillaries, participates in the formation of connective tissue.

Electrospinning uses a high voltage to produce an electrostatic field, which attracts electrically polarized domains of a polymeric solution, from a cone nozzle into a collection area where it solidifies as micro and nanofibres, which makes fiber arrangements, that are agglomerated in three-dimensional structures that can be applied to cell culture. Listed here are some important points to consider in the process of electrospinning:

- The selected solvent must be able to completely dissolve the polymer
- The temperature of the solution and the equipment must be adequate so that evaporation is fast enough to maintain the integrity of the fibers when they reach the collector.

The aim of the present work is the plasma treatment of electrospun fibers of PVA with AA to obtain a biomaterial that can be used as scaffold in tissue engineering, the fibers will be obtained a different temperatures and will be tested in cell culture with HEP-G2 hepatic cells.

#### Experimental

#### **Polymer solutions**

Solutions were prepared of two types of PVA (Aldrich Chemical) The first with 99% degree of hydrolysis and molecular weight in the range of 146.000 to 186.000, high Mw, the second with a degree of hydrolysis of 80% and molecular weight in the interval between 7000 and 9000, low MW. From the first 10 ml of solution were made at a concentration of 0.12 (g / ml) of PVA in distilled water. The solution was prepared at 80  $^{\circ}$  C with constant agitation for 90 minutes, then

allowed to cool to 37 ° C. From the second 10 ml of a solution at a concentration of 0.1 (g / ml) in distilled water were also prepared. The solution was prepared at 80 ° C with constant stirring for 30 minutes, then allowed to cool to 35 ° C. The solution temperature was kept constant during the electrospinning process using a resistive heating element in the form of tape and an autotransformer at 25V. Other solution of the second at the same concentration was also prepared, but 0.33 (g / ml) of ascorbic acid was added.

Electrospinning variables and the temperatures used in the samples are presented in Table 1.

Concentration (g/ml)	Polymer	Electrospinning Temperature (°C)	needle caliber	Voltage (kV)	Distance to collector (cm)	Injection Flux (ml/h)
0.12	PVA 99%					
	High MW	Room (~ 27°)	25G*	18-20	15	
0.1	PVA 88%					
	Low MW					
0.1PVA-0.33 AA	PVA 88%					
	Low MW					
		Controlled 35°	23G*	35-37	20	1.5
0.1 PVA-0.33 AA	PVA 88%					
with PPy	Low MW					

\*needle: 25G = D intern 0.25mm 23G = D intern 0.33mm.

The equipment used for characterization were:

• Optical microscopy: The analysis was performed with a Leica Microscope, Model: DMLP, 100X and 500X with magnifications.

• Scanning Electron Microscopy (SEM) was performed using a JEOL JSM-7600F model

• Inverted microscopy was performed using a microscope Iroscope model 20IFL MG on the fibers, exploring the surface and representative images taken using a Panasonic model WV-cp244.

## Cell Growth procedure:

1. The materials were placed in culture dishes of 35 mm.

2. 2 ml  $(5x10^5 \text{ cells/ml})$  of HepG2 cells were added with growth medium.

3. The cell medium was changed every other day for 15 days.

4. The cells were cultured at a temperature of 37 ° C with 5% CO2 and saturated humidity.

5. Cell proliferation was evaluated on the coverslips on days 2, 4, 8, 11 and 15 of culture, with an inverted microscope.

## **Results and Discussion**

## Scaffolds PVA at 0.12 g/ml

The morphology of the scaffold was very fragile and brittle as shown in Figure 1 (a), having no control of the temperature of the solution; the injection is difficult when it began to cool. The SEM image (Fig. 1b) shows that the fibers are joined together because the fiber does not get dry in to

the collector this means that the sample is fragile, the porosity is maintained but the sample is hard to handle.



(a) (b) Fig 1 .- a) Optical microscopy (50X), PVA membrane 0.12 (g / ml) b) SEM image of PVA Membrane 0.12 with a 100X magnification.

#### Scaffolds PVA 0.1 g / ml

By changing both the concentration and polymer molecular weight, the solubility in water increased, taking 30 minutes to dissolve as compared to 90 minutes of the solution at 0.12 g/ml, also improving the electrospinning process with a lower viscosity helping the injection of the solution. The morphology improved significantly, it was not fragile and brittle, the mechanical properties of the scaffold were better, is more porous (Fig. 2) and the fibers do not agglomerate.



(a) (b) Fig. 2. a) Optical microscopy (500X), PVA membrane at 0.1 g / ml. b) SEM image of PVA Membrane at 0.1 g / ml with a magnification of 500 X.

#### Scaffolds PVA 0.1 g/ml Ascorbic acid 0.33 g/ml

From the membrane obtained,  $0.5 \text{ cm}^2$  were cut and immersed in water, in less than a minute it was dissolved completely, the pH measured in the water end out to be 4, so that the membrane is not a good drug dispenser, since all the drug is abruptly released, with this it is necessary to modify the membrane surface by plasma polymerization of pyrrole.

The surface of the sample PVA-AA was modified by plasma polymerization, used as protective coating or insulating layer, and contributes to the anchor of the cells, which improves the strength characteristics. From the membrane obtained after the plasma treatment,  $0.5 \text{ cm}^2$  were cut and immersed in water and this time it did not dissolve, but the pH was measured immediately and it was 4.



Fig. 3. a) Optical microscopy (100X), PVA membrane 0.1 PVA-0.33 AA. b) SEM image of PVA membrane at 0.1 PVA-0.33 AA. with a magnification of 500 X.

After 1 day the sample was immersed in water, pH was measured, than removed, allowed to dry and the next day did the same, this was done until pH was constant. The following graph and table shows that on day 1, the pH was 4 and with the daily immersions this increase to be constant at 7.



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#### **Cell Culture**

Figure 4 shows the sample at different days of the cell culture. It can be seen that the cells proliferated and anchored, to the surrounding area and pore morphology of the material, taking the shape of control culture; they start with spheroidal shape and as they were adhering to the surface of the material, they began to change to a elongated polyhedral shape and closely linked to each other. It is noteworthy that the culture media does not dissolve the material for a period of 15 days, and it does not undergo in changes in their shape and size so it can presumably be used in this type of media an its behavior is better as compared with the experimental part is immersed in distilled water.



Fig.4 Cell culture on 0.1PVA-0.33 AA g/ml subjected to plasma coating PPy a) 2 days of culture, b) 8 days of culture, c) 10 days d) 15 days of culture

#### Conclusions

The results can be considered as positive, the membranes showed good structure and morphology, pore sizes are adequate to help cell proliferation not only in 2D but in 3D. Drug release, has good interaction and behavior at the cellular level, so that the materials developed have potential to be used as scaffolds in Tissue Engineering.

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## CONSTRUCTION AND EVALUATION OF SCAFFOLDS MODIFIED WITH POLYPYRROLE PLASMA FOR THE GROWTH OF CARTILAGE CELLS

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#### Abstract

Cartilage lesions caused by degenerative joint defects or traumatic injuries is a health problem, due to poor regenerative capacity of cartilage. Then, damaged cartilage is difficult to repair, causing pain, functional disorder and disability with little recovery opportunities even with treatment. Although this is an open subject, there have been some advances by means of tissue engineering, and particularly with the development of new scaffolds for cellular growing, in order to satisfy nowadays needs.

This work continues the research started between Universidad Autónoma Metropolitana and the Hospital Infantil de Mexico "Federico Gómez", where they have try out biodegradable sponges covered with pyrrole and finding out promising results. In this work, each scaffold was generated by electrospinning of synthetic polymers such polylactic acid (PLA), polycaprolactone (PCL) and the combination of both. Many shapes were obtained adjusting the degradation time, and were coated by plasma polymerization (pyrrole/iodine) for the growth of cartilage cells. The scaffolds were evaluated by optical microscopy, scanning electron microscopy (SEM), X-ray spectroscopy energy dispersive (SEM-EDS), in addition to evaluating its composition, size, pore distribution and fiber diameter. Finally, the viability and proliferation of chondrocytes, both in vitro and in vivo, were also studied with encouraging results.

#### Introduction

Tissue engineering is an emerging discipline, which aims to assist and accelerate the regeneration and tissue repair. Providing to cells a local environment that allows their proliferation and differentiation. Surgical techniques are currently used to treat cartilage injuries, where none has been successful in the long term. Recent advances in the development of biomaterials and cell therapy have been offered the chance to explore new strategies, both natural and synthetic materials. Allowing the generation of biomimetic scaffolds constructed from a synthetic scaffold (biodegradable polymer, porous and tube-shaped).[1]

The human body is composed of four tissues: connective, epithelial, muscular and nervous. An example of connective tissue is the cartilage, which is composed of chondrocytes isolated in small areas of the extracellular matrix composed of fibers. Nourished by diffusion and surrounded by a layer of dense collagenous called perichondrium. Classified in three types of cartilage (hyaline, elastic, fibrous) depending on the body region where is located. [2]

The implementation of a technique called electrospinning allows the deposited of fibers made from (PLA/PCL) forming an interconnecting network shaped as a porous material. This technique

has allowed the design of scaffolds with characteristics of layer by layer, allowing more control on the fibers that are deposited. So by varying the composition of PLA/PCL modifies the porosity and pore geometry alter their mechanical properties such as equilibrium and dynamic stiffness.[3] So, modifying the pore size, pore density, biocompatibility, specificity of form, the integration of native tissue and degradation depending on the rate of formation of neo-cartilage. [4] Can obtain a useful model for the development of scaffolds, concluding that the pore architecture affects the amount and composition of cartilage tissue. [5]

## Experimental

We developed a porous polymer scaffold composed of biodegradable and biocompatible (PLA and PCL) polymers by means of electrospinning, coated with a thin film of pyrrole with iodine using plasma polymerization, studying the effects of degradation and biocompatibility in vitro with elastic cartilage cells of rabbit.

**a) Samples preparation**: two solutions were prepared at 12 wt% using as solvent a mixture 2:1 of chloroform and ethanol respectively, the first one of PLA and another of PCL, to obtain fibers under the following procedure:

- 1. Both polymers were dissolved separately in vials, for 12 hrs.
- 2. Both solutions were placed in 20 ml syringes. On electrospinning nozzle team, using different gauge needles. Because of the viscosity of each of the solutions and the molecular weight of each of the polymers.

**b)** Fibers Preparation: Both solutions were placed on the injector to apply pressure on the plunger of the syringe in order to generate a steady flow, collecting the fibers on a grounded conductive surface at a distance of 15 cm. Between the needle and the collector an electric field is generated of about 30 to 35 kV. The solvent evaporates during the flight and fibers with a diameter between 700 nm and 3 microns are obtained. Generating a scaffold with a 70:30 ratio of PLA and PCL.

c) Post-spinning treatment: Prior to the plasma polymerization, the polymer network was placed in a vacuum furnace for 7 days at 42  $^{\circ}$  C, in order to avoid the presence of solvent on the sample, taking into account the glass transition point of the materials (Tg).

**d)** Coating of fiber by plasma: The three-dimensional scaffold generated by polymer fibers is collocated into of a plasma reactor. Making a coating of pyrrole doped with iodine, modifying the surface properties of the fibers. The polypyrrole was synthesized for 1 hr. at intervals of 6 min of pyrrole and 4 min. of iodine.

e) Characterization of the fiber: The material was characterized by evaluating the morphology of the fibers and the pore size by optical microscopy and Scanning Electron Microscopy (SEM). Making an evaluation of average pore size of each of the scaffolds generated from PLA, PCL and the combination of both (PLA/PCL).

i) Material Porosity: For the evaluation of the porosity in the SEM images, the intensity thresholds were established by segmenting the image of interest: porosity of the material and the fibers were established. The porosity in black (256) and the fibers is the background in white (0), detecting the edges of the pores by changing the threshold from 0 to 256 or vice versa. Defining the shape and size of the pores.

e) Obtaining chondrocyte cells and chondrocyte culture: To obtain the elastic auricular cartilage cells and chondrocytes culture:

1. A biopsy of the elastic auricular cartilage was made using a male rabbit of two months. Under aseptic conditions an incision was made on the right ear of the rabbit in the dorsal zone and separating the skin of the cartilage.

2. In a laminar flow hood under sterile conditions, a small piece of cartilage is mechanically disintegrated and placed in a disruptive solution and then allowed to settle and decant the tissue in a collagenase solution, again stirring continuously. Centrifuged and decanting to obtain the cell button and re-suspended it in culture medium supplemented with antibiotic-antifungal to achieve their proliferation.

#### f) Cellular tests:

- 1. In vitro: The cell expansion was initiated on the membranes, growing at a temperature of  $37^{\circ}$  C with 5% CO<sub>2</sub> and saturated humidity. Changing the cell medium every third day for 30 days. Evaluating on the membranes the cell proliferation the day 3, 7, 10 and 30 of culture, with SEM and viability tests (MTT).
- 2. **In vivo**: cells were re suspended and cultured under the same conditions on the membranes, changing the cell medium every other day for seven days. At day 7 implantation was performed in the dorsal region of the rabbit and 30 days after the explant. Evaluated with SEM and MTT tests, the cell proliferation in the membranes.



Figure 1. Scalffods (a) PLA, (b)PCL and (c) combined material PLA/PCL.

#### **Results and Discussion**

Once optimized the electrospinning technique to generate scaffolds of PLA, PCL and combined. The electrospinning conditions were: concentrations12%, preheated chamber at 30  $^{\circ}$  C, chloroform/ethanol and drum rotary picker/displacement. 3 different scaffolds were obtained with different fibers characteristics. Figure 1 shows the PLA fibers having variable diameter, ranging between 2.5 and 15  $\mu$ m. In the case of PCL the observed fibers have a smaller diameter, with a uniform distribution, forming a material with pores with larger area compared to the PLA.

Combining the two polymers to produce a material with fibers combined with porosity similar to those of PLA but with smaller pores. As the smaller-diameter PCL was degraded first giving different biodegradation times in the combined material.

With regard to the number of pores, an average pore of  $18 \ \mu\text{m}^2$  was reported in the combined material, compared to the PLA where the average is  $26 \ \mu\text{m}^2$  and the PCL with average of  $120 \ \mu\text{m}^2$ . Resulting in a decrease in pore size which favors the quantity and composition of cartilage. Post-treatment was performed on the membranes to remove the remaining solvent, the analysis

was made by X-ray with energy dispersive spectroscopy (SEM-EDS), where we pretreated the samples and reported a 0.11% chlorine (Cl) content, which can be toxic to cells. After of the treatment the chlorine was removed of the different scaffolds .



Fig.2 In Vitro culture cells.



Fig. 3 In Vivo implant on the rabbit

In vitro testing was performed on membranes from an elastic auricular cartilage biopsy which was obtained by initiating the primary culture cell expansion with  $4x10^6$  cells, cultured for 3 weeks in order to have a number of confluent cells for testing. For in-vitro testing the cells were resuspended and cultured on the membranes to evaluate their viability (MTT) and cellular distribution by SEM in a total of 30 days. Assessing the days 3, 7, 10 and 30 after sowing, reporting a 73.33% increase in the viability of the membranes at 30 days of planting and pointing up in SEM the presence of some circular-looking cells at 7 days, obtaining cell confluence at 30 days (figure 2).

We performed a rabbit implant in-vivo tests, cells were cultured on membranes for 7 days and implanted in the dorsal region of the rabbit. 5 samples were placed approximately  $1 \text{ cm}^2$ , which were covered with a mesh of vycril before implanting. Making membrane explants after 30 days assessing their viability (MTT) and cellular distribution (SEM) reported a value of 1.0285 compared to in-vitro testing at 30 days was 0.783 (figure 3).

#### Conclusions

A polymer-solvent system was designed that allow obtaining scaffolding through electrospinning of PLA, PCL and the combination of the two polymers. Several evaluated factors favor the formation of fibers by electrospinning, with the best conditions: the temperature increase inside the chamber at 30  $^{\circ}$  C, the concentration of 12% of the polymer, the combination of solvent ethanol/chloroform, and the rotation drum collector. All these factors favor the formation of scaffolds useful in tissue engineering.

We analyzed the characteristics of porous materials in SEM reporting that the combination of both materials gives a uniform porosity, which is suitable for Tissue Engineering. We analyzed the characteristics of porous materials in SEM reporting that the combination of both materials gives a fiber material with uniform porosity, which is suitable for Tissue Engineering.

The post-spinning treatment removed the solvent remaining in the scaffolds. Materials were modified by surface-polymerized in a plasma reactor, coating with a thin film of pyrrole/iodine. In order to promote cell proliferation on scaffolds. Noting that the combination of both materials.

It was decided to test cellular scaffolds (PLA/PCL) from a primary culture to assess cell viability and proliferation of materials. So in-vitro MTT results reported a good performance on the viability of the scaffolds, indicating that the plasma treatment promotes an environment for cell proliferation.

In vivo tests were performed the same animal, reporting feasibility of scaffolding and cell confluence. Early biodegradation was not observed in implanted material, in comparison with previous studies in poly-glycolic acid (PGA) in vivo tests.

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## *N*-VINYLCAPROLACTAM COPOLYMERS AND THEIR pH- AND THERMO-RESPONSIVE PROPERTIES

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#### Abstract

A series of random copolymers of NVCL with *N*-vinyl pyrrolidone (NVP), methacrylic acid (MAA), hexyl acrylate (HA), 2-methacryloyloxybenzoic acid (2MBA) and 2,2'-(diethyl)aminoethyl methacrylate (DEAEM) were synthesized via RAFT. The obtained copolymer composition suggests that the polymerization was random, so it is expected that the co-monomeric units are distributed randomly along the PNVCL chain. It was found that the type of co-monomer and its concentration in the copolymer influences the LCST behavior of PNVCL: In the case of DEAEM, NVP, MAA and 2MBA copolymers the LCST was higher and in the case of HA (hydrophobic polymer) was lower than for PNVCL. Furthermore the copolymers show pH-sensitivity in aqueous solution.

#### Introduction

Water soluble polymers are attractive because they are able to respond to environmental changes, such as pH and temperature. In the case of temperature response, there is a phase separation upon heating, and the system exhibits a lower critical solution temperature (LCST). Poly(N-vinylcaprolactam) (PNVCL) is a thermo-sensitive polymer that has recently attracted a great interest mainly because is stable against hydrolysis, non-toxic, and biocompatible.[1] These properties make it an interesting candidate for biomedical applications.[2,3] Although PNVCL has gain recently much more attention,[5-7] its impact in scientific publications as compared to the most studied temperature sensitive polymer: poly(N-isopropylacrylamide) is still low. This may result from the fact that de N-vinylcaprolactam (NVCL) polymerization is more difficult to achieve and it's less controlled that that of N-isopropylacrylamide (NIPAAm).

Previously, we described the controlled radical polymerization of NVCL via reversible additionfragmentation chain transfer (RAFT) polymerization employing 4-cyano-4-(dodecylsulfanylthiocarbonyl)sulfanyl pentanoic acid as chain transfer agent. It was found that it is possible to obtain the target polymer with acceptable molecular weight and polydispersity.[4] In order to obtain the different types of random copolymers, it is important to use a RAFT agent that can be widely used for different families of monomers, therefore we choose the trithiocarbonate CTA<sub>1</sub>, a RAFT agent with medium chain transfer ability.

Finally the preparation of NVCL copolymers is a desiderable goal in temperature sensitive material science since comonomers usually makes possible to tailor the LCST response of PNVCL as recently shown by conventional free radical copolymerization.[8]

#### Experimental

#### **Polymer synthesis**

For random copolymerizations with NVCL, 1,4-dioxane as solvent, 2,2'-azobis(cyanopentanol) (ACP) as azo initiator and the trithiocarbonate CTA<sub>1</sub>, were used. *N*-vinylpyrrolidone (NVP), hexyl acrylate (HA), methacrylic acid (MAA), 2-(methacryloyloxy)benzoic acid (2MBA) and 2,2'-

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(diethylamino)ethyl methacrylate (DEAEM) were used as co-monomers, maintaining the NVCL content in the recipe always higher than 70%. The reaction conditions, purification and characterization were the same. As an example an experiment of copolymerization with NVP is described below. A mixture of NVCL (1.27 g, 9.1 mmol), NVP (0.048g, 0.48 mmol), CTA1 (0.016 g, 0.042 mmol), ACP (0.004 g, 0.017 mmol) and 1,4-dioxane (4 mL) was transferred to an ampoule containing a magnetic stir bar. The oxygen was removed using three cycles of freeze-vacuum-thaw, and the ampoule was sealed with flame under argon atmosphere. The ampoule was immersed in an oil bath at 90°C with magnetic stirring. After 24 h, the polymerization was stopped by cooling to room temperature. The solvent was removed in vacuum. The purification was carried out by dissolution in the minimum amount of methanol followed by precipitation from diethyl ether and decanting in the case of copolymerization with DEAEM the precipitation was carried out with petroleum ether. This procedure was repeated three times to remove residual monomer followed by drying under vacuum. The polymerization yield was obtained gravimetrically.

#### Measurements

The molecular weight and molecular weight distribution were determined by gel permeation chromatography (GPC). The measurements were performed in a solution of dimethylformamide with lithium bromide 20 mM at 40 °C. The dn/dc = 0.0701 value was measured for PNVCL in DMF using a differential refractometer. The phase behavior (LCST) was determined by turbidimetry on a DR/890 portable colorimeter and confirmed by dynamic light scattering (DLS) on a Zetasizer NanoSZ. 1w% (Co)polymer solutions in buffers of different pH-values were prepared by stirring in ultrasonic bath followed by stirring and filtrated before measurement using 0.45 microns nylon filters.

#### **Results and Discussion**

The goal of this investigation was to prepare random copolymers of NVCL with various comonomers in a straightforward fashion and controlling its incorporation. For this goal, it was important to use a RAFT agent that can be widely used for different families of monomers, therefore we choose trithiocarbonates, CTA's with medium chain transfer ability. The comonomers and CTA used in this study are despicted in Figure 1. NVCL was random copolymerized with hydrophobic (HA), hydrophilic (NVP), basic (DEAEM) and acid comonomers (MAA and 2MBA) to see the effect in the LCST of PNVCL. All copolymers were prepared seeking a mayority content of NVCL. In the case of NVP and DEAEM, they were random copolymerized changing the co-monomer content to 5, 10 and 15mol%. On the other hand HA, MAA and 2MBA were random copolymerized with NVCL using a comonomer content of 5mol%. The theoretical molecular weight was calculated using the ideal RAFT polymerization equation assuming full incorporation of monomers onto polymer.

The results of the random copolymerization are shown in Table 1.



Figure 1. Structures of co-monomers and CTA used in random copolymerization with NVCL.

Sample	Copolymer	co-mon compos. %	yield (%)	$\begin{array}{c} M_{n,}(target) \\ \left(g/mol\right)^{b} \end{array}$	$M_n$ (g/mol) <sup>c</sup>	$M_w/M_n^{\ c}$
	PNVCL	_	43.1	13,800	18,400	1.28
1	poly(NVCLcoNVP <sub>5%</sub> )	3.1	45.3	32,100	27,600	1.19
2	poly(NVCLcoNVP <sub>10%</sub> )	9.2	47.9	31,400	25,400	1.14
3	poly(NVCLcoNVP <sub>15%</sub> )	15.2	47.7	31,000	20,800	1.22
4	poly(NVCLcoDEAEM <sub>5%</sub> )	19.2	16.4	32,500	20,600	1.26
5	poly(NVCLcoDEAEM <sub>10%</sub> )	22.1	17.7	33,100	33,100	1.41
6	poly(NVCLcoDEAEM <sub>15%</sub> )	27.0	28.8	33,600	27,600	1.53
7	poly(NVCLcoMAA <sub>5%</sub> )	2.5	19.4	31,000	51,300	1.17
8	poly(NVCLco2MBA <sub>5%</sub> )	4.6	13.9	32,800	14,500	1.20
9	poly(NVCLcoHA <sub>5%</sub> )	5.0	46.0	32,600	25,000	1.48

Table 1. Random copolymerization of NVCL.<sup>a</sup>

<sup>a</sup>Polymerization at 2.4 monomer concentration in 1,4-dioxane at 90 °C in 24 h.

<sup>b</sup>The target molecular weight was calculated at 100% conversion.

<sup>c</sup>By GPC in DMF+LiBr 0.02 M at 40°C.

As it can be seen at Table 1, the obtained copolymer composition suggests that the polymerization was random, so we expect that the co-monomeric units are distributed randomly along the PNVCL chain. The co-monomer compositions obtained in the random copolymers with DEAEM was higher than the target compositions. It can be also seen when NVCL is copolymerized randomly with the basic (DEAEM) and acids co-monomers (MAA, 2MBA) the yield decrease (compared with PNVCL) while when it is copolymerized with hydrophobic (HA) and hydrophilic (NVP) the yield remains unchanged.

In Table 2 the LCST determined for the random copolymers at physiological pH (7.4) is shown. As can be seen, in all cases the incorporation of a co-monomer modifies dramatically the LCST of PNVCL.

Sample	Polymer	pH 7.4 (°C)
	PNVCL	32
1	poly(NVCLcoNVP <sub>3.1%</sub> )	36
2	poly(NVCLcoNVP <sub>9.2%</sub> )	36
3	poly(NVCLcoNVP <sub>15.2%</sub> )	38
4	poly(NVCLcoDEAEM <sub>19.2%</sub> )	42
5	poly(NVCLcoDEAEM <sub>22.1%</sub> )	58
6	poly(NVCLcoDEAEM <sub>27%</sub> )	36
7	poly(NVCLcoMAA <sub>2.5%</sub> )	38
8	poly(NVCLco2MBA <sub>4.6%</sub> )	44
9	poly(NVCLcoHA <sub>5%</sub> )	27

Table 2. LCST of random copolymers at physiological pH (7.4).

In the case of the hydrophilic NVP (with a similar structure that NVCL) the LCST increased as a function of NVP content. In the case of DEAEM, samples 4, 5 and 6, the LCST is always higher than PNVCL; however there is not a clear trend with comonomer content. PDEAEM has a pKa close to 7.0, so at pH 7.4 less than 50% of the units are ionized and the diethyl-radicals are hydrophobic. A study at different pH values is needed to shed more light into this behavior. In the case of the copolymers containing acid comonomers, samples 7 and 8, we can see that acid co-monomers increased the LCST since the pH (7.4) is above the pKa of those acids. As expected, the hydrophobic comonomer HA results in a drop of LCST value. Finally we can see with the results that the change of LCST in the copolymer also depends of the co-monomer content.

#### Conclusions

It was possible to obtained random copolymers of PNVCL via RAFT with acceptable molecular weight and polydispersity.

The type of comonomer and its concentration in the copolymer influence the LCST behavior of PNVCL. It is possible to increase the LCST (with NVP or acid comonomers at pH 7.4) or to decrease its value with hydrophobic comonomers (HA).

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#### Biomaterial based on chitosan for auricular neocartilage using autologous cell

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Reconstruction of cartilage of the pinna continues to be a challenge in reconstructive surgery. In Mexico, 1 of 1500 children suffers microtia [1]. Biomaterials based on chitosan (CTS) and Poly vinyl alcohol (PVA) show great potential for the creation of synthetic cartilage [2]. The study goals were: to engineer a biosynthetic construct using CTS-PVA blends seeded with auricular cartilage; to study the feasibility of culture and proliferation of cells from auricular cartilage (AC) in 3D, and to compare the citology and immunocitochemical composition of engineered constructs. Pediatric auricular cartilage was collected. CTS and PVA were crosslinked with epichlorohydrin (ECH) and seeded with isolated cells from AC; the construct was cultured. Cells had normal auricular morphological features and adhered to the polymer CTS-PVA-ECH. Constructs were positive to cartilage proteins. These results demonstrate the feasibility of tissue-engineered cartilage as a potential graft material for the treatment of microtia.

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## HYDROLYTIC DEGRADATION OF POLYESTERAMIDES BASED ON $\epsilon$ -CAPROLACTONE

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The hydrolytic degradation of aliphatic polyesteramides based on  $\varepsilon$ - caprolactone is described. The ring-opening polymerization of  $\varepsilon$ -caprolactone was carried out in the presence of ammonium molybdate tetrahydrate and using aliphatic amines (butylamine, hexylamine, octylamine, decylamine, dodecylamine and benzylamine) as co-initiators in bulk at 150 °C. Molecular weights of the obtained polyesters were in the range of 1700-2000 Da. Obtained polyesteramides (1 g) were placed in a 50 ml round-bottom flask containing NaOH solution (20 ml, 10%), p-toluenesulfonic acid (20 ml, 500 mM) and Ringer solution respectively, and reflux with stirring for 2 hr. After 2 hr the remaining samples were removed from the flask, washed with distilled water and cold methanol and left to dry at room temperature under ambient conditions for one night. The dried polymer was weighted, and degree of degradation was estimated from the mass loss. It was observed that degradation was favored when alkaline medium was used. Structural changes in the degraded polymers were determined using FT-IR.

## ENZYMATIC SYNTHESIS OF POLYESTERAMIDES BASED ON $\delta\text{-VALEROLACTONE}$

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The enzymatic ring-opening polymerization of  $\delta$ -valerolactone ( $\delta$ -VL) in the presence of aliphatic amines at 120°C is described. Polymerizations were carried out with immobilized lipase of *Yarrowia lipolytica* (YLL) and tin (II) 2-ethylhexanoate as catalysts respectively. Polyesteramides were characterized by <sup>1</sup>H and <sup>13</sup>C-NMR, FT-IR and differential scanning calorimetry (DSC). Molecular weights in the range of 618-2500 Da and conversions of 34-61% (determined by <sup>1</sup>H-NMR) were observed. It was observed that immobilized lipases in Lewatit VP-OC1026 YLL are more efficient in the enzymatic ring-opening polymerization of  $\delta$ -VL than those immobilized in Amberlyst15. Depending on the length of the aliphatic amine, the molecular weight of the polymer decreases but conversions and reaction rates increase. When tin (II) 2-ethylhexanoate is used, a shorter reaction rate is observed.

#### ENVIRONMENTALLY FRIENDLY POLYESTER-URETHANE FILMS: PREPARATION, CHARACTERIZATION, AND MECHANICAL PROPERTIES

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The enzymatic synthesis of  $\alpha$ - $\omega$  telechelic polycaprolactone diols (HOPCLOH) was studied. Synthesis of  $\alpha$ , $\omega$ - telechelic PCL diols was achieved by enzymatic ring opening polymerization with *Yarrowia lipolytica* lipase immobilized on macroporous resins (Lewatit VP OC 1026, Lewatit K2629 and amberlyst15) and using triethyleneglycol, 1,3-propanediol, tetraethyleneglycol, 1,6-hexanediol and 1,8-octanediol as initiators. Biodegradable linear poly ester-urethanes were prepared from synthesized PCL diols and hexamethylenediisocianate (HDI). Depending on the length of PCL in HOPCLOH, the polymers were amorphous or semicrystalline. The polyester-urethanes containing triethyleneglycol, 1, 3-propanediol and 1, 6-hexanediol showed elastomeric behaviour with very good mechanical properties.

# EFFECT OF THE ADDITION OF SPHERES OF CHITOSAN/NAOH (UNWASHED) IN THE SWELLING OF AN ACRYLAMIDE POLYMER MATRIX

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The chemical composition of a hydrogel is of vital importance in the design and control of their physical and chemical properties. Usually, the increase in the proportion of highly hydrophilic monomer leads to hydrogels with a higher degree of swelling, but with poor mechanical properties. However, for many biomedical properties applications require hydrogels with a high swelling capacity and good mechanical properties. This can be resolved by adding a more hydrophobic monomer, which while reducing the water content in the hydrogel (usually decreases its biocompatibility), improves the consistency of the material and their mechanical properties. Due to this there is a need to synthesize hydrogels that do not dimisnish its biocompatibility, it is proposed the incroporation of chitosan in the polymer network. It is known that polyacrylamide and chitosan can form interpenetrating networks, however, no studies have been reported where the chitosan is added in the form of spheres for drug delivery.

The mechanisms of swelling-sensitive pH changes involving protonation of the amino group of chitosan when the pH decreases. This protonation leads to the repulsion of the chain, the diffusion of protons and counterions, and the dissociation of secondary interactions. This dissociation may explain the high degree of swelling of a hydrogel semi-interpenetrated (the hydrogel matrix composed of a cross-linked and one monomer without crosslinking within that network). The semi-and fully interpenetrating networks are highly versatile because they have a high degree of swelling.

# SILICA GEL MATRIX AND A RECOMBINANT ENZYME (rLAP), A NOVEL BIOPOLYMER FOR PHARMACEUTICAL USE

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Due to the properties of reversibility and volume changes of polymer gels, there is interest in developing biopolymer systems cappable to adapt to response of biochemical changes of enzymatic reactions, i.e. proteins having different bio-affinity. Leucine aminopeptidase recombinant (rLAP) is an enzyme, whose gene is obtained from the bacterium *Vibrio proteolyticus* expressed in *Escherichia coli*. rLAP and is used in the process of removal of N-terminal methionine in the purification steps of recombinant human proteins for pharmaceutical use [1].

This work, aims to covalently immobilize the rLAP supported in a polymeric silica gel, to allows a continuous process of removing N-terminal methionine for the production of interferon. In the preparation of polymer gel a precursor tetraethyl orthosilicate (TEOS), HCl as a catalyst, ethanol and water were used. In order to activate the silica gel, 3-aminopropiltrietoxilano was used. The activation involve the incorporation of amino groups on the surface of the support; also glutaraldehyde formed Schiff bases which allow for covalent bonding between the amino groups of the silica support and the amino groups of the enzyme surface [2,3]. Once enzyme was immobilized in the silica gel support, their catalytic activity was determined using synthetic substrates (L-leucine-p-nitroanilide) in order to understand the catalytic efficiency of rLAP.

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### KINETICS OF DMAEMA POLYMERIZATION IN MICROEMULSION TO PREPARE SMART NANOGELS

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Polymers, which can react, adjust or modulate their physicochemical character, in response to an external stimulus, are generally referred to as smart or stimuli-responsive polymers. Recent interest in these systems focuses on hydrogels because of their tunable chemical and three-dimensional physical structure, high water content and biocompatibility. Hydrogels can be in the form of macroscopic networks or confined to smaller dimensions such as nanogels. Nanogels particles are faster in responding to changes in their environment than macroscopic or bulk counterparts gels for agrochemical, medical or sensor applications due to their much higher interfacial area for rates multivalent bio-conjugation and greater exchange [1, 2]. Polv(N. N' dimethylaminoethylmethacrylate) (PDMAEMA) is a cationic polyelectrolyte that has been shown to be both temperature and pH sensitive [3, 4].

The objective of this report is to present the results of a kinetics study of the DMAEMA polymerization in a normal microemulsion. The independent variables considered were temperature (60 to 80 °C), initiator concentration (4.75e-04 to 14.25e-04 moles), reaction time (120 to 300 min) and the molar ratio of DMAEMA to surfactant employed (1.175 to 3.525). The microemulsion polymerization of DMAEMA yielded transparent and yellowish nanogels with conversions between 69.7 and 95.8 % (w/w) and average particle diameters from 9.5 to 86.5 nm. The complete results of the experimental design would be presented and discussed.

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#### Abstract

The spray-drying process has been used to encapsulate food ingredients such as antioxidants. The objective of this work was to produce microcapsules of gallic acid, a phenolic compound that acts as antioxidant, by spray drying with aqueous extract of nopal mucilage (Ofi) as encapsulating agent and characterize the rheological response and the particle size distribution of reconstituted encapsulated solutions at 6%(w/v). The drying parameters studied were: inlet air temperature (130 and 170 °C) and speed atomization (14,000 and 20,000 rpm). The rehydrated biopolymer showed a non-Newtonian pseudoplastic behaviour. The cross model was used to model the rheological data. Values for "m" varied between 0.55 and 0.85, and for " $\lambda$ ", between 0.0071 and 0.021 s. The mechanical spectra showed that sample with gallic acid is stable at long times and presents a bimodal particle size distribution. This study demonstrated the effectiveness of nopal mucilage to be used as wall biomaterial in microencapsulation by the spray drying process.

#### **1. Introduction**

Polyphenols are chemical compounds or phytochemicals with diverse biological activities, based on their antioxidant capacity Cho et al. (2011) suggest that ingestion of polyphenols rich food is beneficial to human health. Gallic acid (acid 3, 4, 5-tri-hydroxy-benzoic) and its derivatives are considered natural antioxidants and their effects and uses have been widely reported (Pasanphan & Chirachanchai, 2008; Negih et al., 2005). Spray drying is a common technique for producing encapsulated food materials (Sáenz et al., 2009). Good microencapsulation efficiency during spray drying is achieved when the maximum amount of core material is encapsulated inside the powder particles, succeeding in microcapsule stability, volatile losses prevention, and product shelf-life extension (Seid et al., 2008). High moisture content in the mucilage limits its applications, generating the need for previous treatments such as spray drying (SD) to increase its potential uses. The SD process is notorious for providing good material properties (low moisture, short residence times, relatively low temperatures, and retention of solute or bioactive compounds) (Perry & Green, 2003). In this work, an antioxidant compound such as gallic acid was encapsulated using aqueous extracts from Opuntia ficus indica (Ofi) mucilage (fresh and reconstituted) as wall material by spray drying; the biomechanical response in simple shear and oscillatory flow, the particle size distribution (PSD), and differential scanning calorimetry (DSC) of samples were evaluated and analized. The thermal and microstructure results were used to evaluate and measure the effectiveness of this material (aqueous extracts from Ofi) as an encapsulating agent and its role in the functional and final rheological properties. Consequently, the time-temperature response through DSC coupled with scanning electron microscopy (SEM) measurements was evaluated as the possibility for this encapsulating process. The microcapsules obtained represent an interesting option for food antioxidants and additives incorporation into functional industrial applications.

#### 2. Materials and methods

2.1. Materials: Cladodes of nopal (*Opuntia ficus indica*) (*Ofi*) of approximately 6 months old plants, with 92.21% moisture content, were collected randomly from the same plantation (March 2011), at Milpa Alta, Mexico City. The moisture content of fresh cladodes was determined with an infrared balance (AND, model AD-4714A). Cladodes were washed thoroughly with water at 25°C, using a plastic bristle brush. Cladodes were macerated (500 mL deionized water per kg of material) to facilitate the extraction of mucilage

2.2. Spray drying: A pilot scale spray dryer co-current flow Niro atomizer (Production Minor Spray Dryer, Niro Inc., Denmark) (Niro, Copenhagen, Denmark), equipped with rotary atomizer (TS-Minor, M02/A) was used to encapsulate. The feed flow was controlled with a peristaltic pump. Distilled water at room temperature was used to stabilize the equipment. Encapsulated samples prepared with fresh mucilage were dried under the inlet air temperature (Ti), and spray atomization speed (Sa) conditions shown in Table 1.

Table 1. Samples drying conditions.							
_	Treatment	Ti (°C)	Sa (rpm)				
_	E1	130	14000				
	E2	130	20000				
	E3	170	14000				
	E4	170	20000				
	E5	130	14000				
	B1	130	14000				
	B2	170	20000				
	B3	130	14000				

2.3. Rheological measurements: Rheological characterization of encapsulated samples was

performed in simple shear flow and oscillatory shear flow, using a controlled stress rheometer (Model AR-G2 TA Instruments) with the concentric cylinders geometry.

2.3.1. Effects of spray drying conditions on steady shear rate flow: Rheological parameters in simple shear flow were performed in strain rate of 0.1 to 300 1/s. Experimental data of the reconstituted mucilage solutions were adjusted properly to the Cross model, expressed in the equation:

$$\frac{\eta - \eta_{\infty}}{\eta_0 - \eta_{\infty}} = \frac{1}{1 + \left(\lambda \dot{\gamma}\right)^m}$$

where,  $\eta$  is shear viscosity (Pa.s), is shear rate (s-1),  $\lambda$  is a relaxation time (s), m is the index flow [m=1-n] (adimentional), and  $\eta_{\alpha}$  and  $\eta_{0}$  are the limit viscosities at high and low shear rate, respectibly (Medina-Torrres, *et al.*, 2000).

2.3.2 Steady oscillatory flow measurements: The viscoelastic properties, storage modulus (G') and loss modulus (G'') were determined through small amplitude oscillatory shear flow experiments at frequencies ranging from 1 to 100 rad/s. Prior to any dynamic experiments, a strain sweep test at a constant frequency of 10 Hz was performed, fixing the upper limit of the linear viscoelastic zone at a strain value of 30% (which was used in all dynamic tests).

2.4. Particle size distribution of mucilage powders (PSD):Particle size distributions (PSD) of the reconstituted mucilage solutions (6% w/v) were quantified with a Mastersizer 2000 laser diffraction particle analyzer (Malvern Instrument Ltd, U.K.). The dispersant was deionized water (particle R.I. = 1.336, and dispersant R.I. = 1.33).

2.5 Differential Scanning Calorimetry (DSC): DSC analysis was performed in a DSC-7 calorimeter (Perkin Elmer, Norwalk, CT, E.U.A.), previously calibrated with Indium and

Second US-Mexico Meeting "Advanced Polymer Science" and XXIV SPM National Congress Riviera Maya, Q. Roo, México. December 2011 equipped with Perkin Elmer DSC pan cells 02190062. An empty pan was used as reference to develop the baseline from 20 to 140°C. The sample (18  $\pm$  0.6 mg), previously weighted in aluminum pans, was initially heated to 80°C for 30 min in the corresponding thermocell of the DSC. In all stages the heating rate used was 5°C/min.

2.6 Scanning Electron Microscopy (SEM): The structure of microcapsules obtained at optimal conditions was studied by SEM. Sample preparation for SEM measurements have been described elsewhere (Medina-Torres *et al.*, 2011). The images were obtained with an electron microscope Leica Stereoscan S420i (Cambridge, England).

## 3. Results and discussion

## 3.1. Effects of spray drying conditions on steady shear rate flow

The effect of each SD factor on the viscous behaviour was studied graphically, comparing the samples with one degree of freedom (L=1), i.e., temperature, pressure or rotor speed. Drying temperature and pressure (rotor speed) were found as the factors that influence the most on viscous behaviour.

3.1.1 Effect of inlet air temperature: Drying inlet air temperature (Ti) was shown to affect the viscosity of reconstituted samples, by increasing Ti, the viscous response was found to decrease as shown in Fig. 1, which shows flow curves from samples B1, E1 and E3. The viscous response of B1 is the highest;  $\eta$  in E1 is greater than in E3. The effect of Ti may be attributed to material thermal degradation when exposed to high temperature; León-Martínez et al. (2011) mentioned that an increase in inlet drying temperature results in thermal degradation and oxidation. High temperature increases cause thermal degradation of the mucilage molecular structure and a lower viscosity.

3.1.2. Effect of air pressure (rotor speed): Viscous response was also found to be affected by spray speed (Sa), where a high speed (20000 rpm) causes the fluid fed into the dryer to exhibit a decrease in viscosity as shown by the flow curves of B1, E1 and E2 samples on Fig. 1. The viscosity  $\eta$  of E1 is higher than E2. Theoretically, rotor speed is proportional to the particle size distribution of mucilage powders obtained. This means that at higher fragmentation rate, greater the contact surface between the drop and hot air, and thus thinner and more porous particles are obtained by incorporation of air with lower moisture content. León-Martínez et al. (2011) suggest that viscosity increases due to the presence of very small particles, causing more particle-particle interactions and increasing the flow resistance, especially at higher shear rates.

3.2. Oscillatory shear curves on spray drying conditions

The effect of drying conditions in storage (G') and loss (G") dynamic modulus of samples prepared with fresh mucilage (B1, E1, E2 and E3), is presented in Fig 2, which depends on frequency, and is a characteristic of the random coil configuration of polymeric networks (Medina-Torres *et al.*, 2000). However at 130°C, there is a slight "solid like" response, implying a higher physical interaction of components (mucilage-gallic acid) and in principle a more stable matrix. León-Martínez *et al.* (2011) suggest a similar effect of spray dried *Ofi* mucilage due to partial hydrolysis of mucilage pectin chains.



**Fig. 1.** Effect of spray-drying conditions on viscosity of samples prepared with fresh mucilage



**Fig. 2.** Effect of spray-drying conditions in storage (G') and loss (G") modulus of samples with fresh mucilage.

*3.3. Particle size distribution (PSD)*: The particle size distribution (PSD) was performed on reconstituted mucilage solutions (spray drying). The PSD have an effect on rheological properties, reflected primarily in viscosity. It is known that rotary atomizers generally produce larger particles compared with spray nozzles, which produces fine particle sizes due to the rotor speed in contact with the fluid (Walton & Mumford, 1999). Fig. 3 shows the PSD from encapsulated samples.

3.4. Scanning electron microscopy: Scanning electron microphotographs for the Ofi (B3) and gallic acid (E5) systems investigated at two water activities ( $0.2 < a_w < 0.4$ ) are shown in Fig. 4. The microphotographs show clearly the microcapsules for the mucilage alone and the mucilage added with gallic acid, respectively. The microcapsules with encapsulating agents were irregularly spherical in shape with an extensively dented surface. The formation of these dented surfaces on spray dried particles was attributed to the shrinkage of the particles during the drying process (Loksuwan, J., 2007).



**Fig. 3.** Particle size distribution of encapsulated samples.



**Fig. 4.** Micrographs of mucilage and encapsulated at 1000 X,  $a_w = 0.2$  (A and C), hydrated  $a_w = 0.4$  (B and D). Samples of treatment B3 are A and B, to E5, C and D.

#### 4. Conclusions

This study has shown that using spray drying to process *Opuntia ficus-indica* mucilage produces a stable powder that has a smaller particle size and, consequently higher viscosity, it also exhibits higher resistance to flow, mainly due to encapsulated systems. Then, the viscous modulus G' predominate over the elastic modulus G' for the spray-dried samples at concentrations  $\leq 6 \%$  (w/v), and showed in some case "solid-like" character, indicating a strong interaction biopolymer- gallic acid. Thus, the viscosity and viscoelastic properties (G' and G") were significantly affected by high inlet air temperatures and behaviour under steady flow for all systems was non-Newtonian shear thinning (n<1). This study showed that samples can achieve stability during storage and subsequent use with reconstituted mucilage, and dried at 130°C and 14000 rpm, and also samples prepared with fresh mucilage, and dried at 130°C and 20000 rpm. The rheological properties were affected inversely by the increase in inlet temperature and the atomizer speed, and directly by the increase of feed flow rate. The nopal mucilage microcapsules described in this study represent a promising food additive for incorporation into functional foods. The SEM data obtained it is proposed that nopal mucilage is an effective encapsulating agent on bioactive functional foods, providing additional structure.

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# EFFECTS OF THERMAL TREATMENTS ON THE POLYMERIC EXOSKELETON OF TWO BLACK CORAL SPECIES

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Antipathes caribbeana and Antipathes pennacea are black coral species commonly are found at deep reefs of Cozumel Island (western Caribbean) whose branched tree-like exoskeleton are composed primarily of chitin fibrils incorporated in a lipoproteic matrix. The arrangement of the constituents of these materials provides a structure with outstanding physical properties [1].

Biopolymers, in particular chitin, are susceptible of structural changes due to temperature treatments. The thermal properties of chitin are determined by several factors: source and sample type, water content, degree of deacetylation, heating rate and atmosphere, the crystalline structure, etc. [2-4]

In this work, the structural properties of the exoskeletons of A. caribbeana and A. pennacea species are explored by means of thermal treatments in the range from room temperature up to 400 °C and the subsequent analysis using X-ray diffraction (XRD), infrared spectroscopy (FTIR) and thermal analysis (DSC/TGA). The effects of thermal treatment from room temperature up to around 210°C induce the enhancement of the bands in the FTIR spectra and x-ray diffractograms, above that temperature, the FTIR and x-ray peaks become strongly attenuated. These effects are specially observed in the infrared bands associated to chitin at 3298 cm-1 and to the secondary amide stretching around 1663 cm-1, in particular allowing the identification of the  $\alpha$ -chitin in the black coral. X- ray diffraction shows that the crystallinity index of the black coral chitin at room temperature is 24% and grows when the temperature increases, reaching a maximum value of 37 % at 210°C and decreases for higher temperatures. Additionally DSC and TGA measurements allowed identifying the most important transformation stages during the thermal treatments, namely evaporation of water and the beginning and progress of degradation, depolymerization and denaturation processes and finally, the degradation of the main functional groups of coral skeleton and coral chitin, in which the polysaccharide structure of chitin is depolymerised and the protein matrix is denatured.

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#### UTILIZATION OF POLYSACCHARIDES FROM BONE OF AVOCADO TO OBTAIN NEW HYDROPHILIC MATERIALS

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In this work we report the use of polysaccharides extracted from the bone of *Persea Americana* var. Hass (commonly known as avocado), which is considered a waste byproduct in the transformation process of avocado in the food industry, lacking of a whole utilization. The *Persea Aamericana* var. Hass is the most common of the varieties grown in Mexico, mainly in the state of Michoacan (whose represents about 80% of national production), and it is of greater economic importance. It has been reported that the bone contains compounds such as polysaccharides, polyphenols, flavofenos, terpenes, terpenoids, among others. The polysaccharides are the compounds that represent the largest proportion, approximately 40 to 60% of extractable materials. Hydrogels were obtained by varying the rate among polysaccharides and the acrylic acid amount, using glycerol diacrylate as cross-linker; the polimerization was realized by redox initiation with sodium metabisulfite and potassium persulfate as redox pair. The hydrogels were characterized by Raman spectroscopy and scanning electron microscopy, meanwhile swelling kinetics was evaluated by gravimetry.
## SCAFFOLD PREPARATION FROM POLYCAPROLACTONE FOR USE IN HUMAN TISSUE SUPPORT

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In tissue engineering, the scaffold with controlled porosity constitutes the base for the physical support of cell adhesion and growth. In this work, scaffolds of polycaprolactone were synthesized by a modified particle leaching method in order to control porosity and pore interconnectivity; the aim is to observe their influence on the mechanical properties and, in the future, on cell adhesion and proliferation rates. PEMA pearls with an average diameter of 150 $\mu$ m were sintered with different compression and temperature in order to obtain the mold. Then the melt polycaprolactone was injected into the porous mold under nitrogen pressure in a custom made device. After cooling and solidifying of the melt polymer, the porogen was removed by selective dissolution in ethanol. The porosity and morphology of the scaffold were studied. Because of their interesting properties and interconnected structure, these scaffolds are expected to find useful applications as a cartilage or bone repair material. [1,2,3,4]

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# SYNTHESIS AND CHARACTERIZATION OF CRYOGELS FROM CHITOSAN

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### Abstract

Heavy metals are considered among the most problematic pollutants in the aquatic environment, as they usually are not removed by natural processes as with occurs some organic pollutants and can enter food chains through processes of bioaccumulation, bioconcentration and biomagnification. One of these metals is copper [1].

In recent years, has begun studying the use of adsorbents of biological origin, as metal adsorbents [2]. This work is derived from a project which proposes the use of chitosan to synthesize cryogels with the aim of having a macroporous structure and with microchannels; likewise be seeks that the cryogels obtained in principle, will be materials stable and resistant to interaction with aqueous solutions, so that can be used in metal sorption processes.

The synthesis was performed using the methodology ISISA; used as crosslinker ethylene glycol diglycidyl ether (EGDE). We considered two levels of amount of crosslinker, and speed of formation of materials.

The characterization consisted in evaluating if the cryogels showed or not solubility in aqueous solutions; to the couple was determined the degree of swelling of the same. Finally, to confirm the obtention of a porous material and the presence of functional groups characteristic of the raw materials that were synthesized cryogels, techniques were used for SEM and FTIR spectroscopy. The results of the synthesis and characterization are presented in this paper.

### Introduction

Among the most problematic pollutants of the water they are heavy metals, which due to their chemical transformations and as they are not easily biodegradable like some organic contaminants, can enter food chains through bioaccumulation processes, bioconcentration and biomagnification, causing major environmental impacts, health, among others. One of these metals is copper.

The adsorption is, by far the most versatile method and is widely used for the recovery of metals from aqueous effluents. The majority of the materials used in this method, are synthetic polymers, so that their biocompatibility and their biodegradability are much more limited than in the natural polymers, that have excellent properties such as biocompatibility, biodegradability, non-toxicity, among others [2]. One of these natural polymers is chitosan, since due to the presence of amino and hydroxyl groups in its structure, is able to interact and form complexes with metal ions.

One of the routes to obtaining metal's adsorbent materials can be the synthesis of cryogels. The present work is derived from a project which proposes the synthesis of cryogels from chitosan, which are crosslinked with ethylene glycol diglycidyl ether, to obtain a stable, porous and resistant material to interaction with aqueous solutions.

The materials obtained were characterized, first determining their solubility in aqueous solutions, to the pair is determined the degree of swelling of the same. Finally to know the surface morphology and the functional groups characteristic of the cryogel, were used SEM techniques and FTIR spectroscopy.

# Synthesis of cryogel

To obtain the cryogels evaluated, first prepare a solution of chitosan (Q), using medium molecular weight chitosan SIGMA-ALDRICH, with a percentage of deacetylation of 75-85% and a solution of acetic acid at 3%, with constant stirring at 65  $^{\circ}$  C for 4hrs.

Later, proceeds to the addition of crosslinking agent ethylene glycol diglycidyl ether (E); were used two levels of crosslinking, 1 and 2%. The reaction is performed in an inert atmosphere, with constant stirring and at ambient temperature.

The latter solution is subjected to cryogenic process ISISA (Ice Segregation Induced Self-Assembly), this procedure consists the unidirectional freezing at constant speed in a liquid nitrogen bath, of a hydrogel, followed by a drying process, which in this case was lyophilization. For the ISISA process, were used two immersion speeds: 6 and 3mm/min (V2 and V1, respectively).

Finally, was performed a washing of cryogels to remove the majority of inert material present in these, which consisted of put in contacting the cryogels with acetic acid at 1.5% and then with deionized water, until it reaches the pH of this, with constant stirring at 30 ° C.

The identification used for each of the cryogels evaluated are shown in table 1:

Crosslinking agent	Percentage of cross linking	Immersion speed	Identification Code
Chitosan	00/	3mm/min	QV1
	0%	6mm/min	QV2
	104	3mm/min	QE1V1
Ethylene glycol diglycidyl	1 70	6mm/min	QE1V2
enter	2%	3mm/min	QE2V1
		6mm/min	QE2V2

## 1. Identification Code

# **Characterization test**

# A. Solubility.

To know the stability of cryogels in aqueous solutions, were put in contact with deionized water (25mL) and constant stirring at 30  $^{\circ}$  C, chitosan cryogels without cross-linking and cross-linked with ethylene glycol diglycidyl ether, for 24 hours, at the end of which was observed if the cryogels maintained its structural stability or were amorphous and / or dissolved in the aqueous medium.

# B. Degree swelling.

The swelling study was carried out gravimetrically measured water gain. A sample of cryogels was taken and immersed in deionized water; at a given time was removed, and carefully dried

surface with a filter paper, to remove excess fluid and weighed; the above was done until it obtained a constant weight. The degree of swelling was reported using the following equation:

$$W_p = \frac{P_h - P_s}{P_s} * 100$$

Where;  $P_h$  is the wet weight of cryogel,  $P_s$  is the dry weight of cryogel and  $W_p$  is the percentage of swelling.

## C. Scanning Electron Microscopy.

To observe the morphology of the material synthesized, was taken a sampled of cryogel and used a scanning electron microscope equipped with a mechanism of high and low vacuum, allowing the analysis of dehydrated and hydrated samples. The structure of the samples were analyzed under vacuum uncoated, at points, the images were digitally captured directly from the equipment.

## D. FTIR spectroscopy.

This test was performed by analyzing a sample of cryogel in a spectrophotometer Fourier transform infrared, in a range of 4000 to 400 cm-1 in transmittance mode. The spectra obtained were captured for subsequent analysis of the bands of compounds present and their interactions. The purpose of the test was to identify functional groups characteristic of the materials being used. Looking to find observe the characteristic bands of the links C = O for the aldehyde group(RCH2 = O) of the crosslinking agent and the molecule of the biopolymer (as NH, CH, among others).

## **Results and Discussion**

## A. Solubility.

In Figure 1 is shows the results obtained from the solubility tests for cryogels QE1V1, QE1V2, QE2V1, QE2V2 and chitosan without cross-linking (QV1 and QV2). It is noted that all cross-linked cryogels were insoluble (or stable) in deionized water; and this resistance is provided by the links produced in the crosslinking of chitosan (Q) with ethylene glycol diglycidyl ether (E), as can be seen with instability submitted by the cryogels without cross-linking, which came after five minutes of contact with water



showing instability at its ends, after 4hrs was almost miscible with water, finally after 24 hours had fully diluted.

# B. Degree swelling.

The percentage of swelling at different times is shown in Figure 2, which shows the behavior of cryogels QE1V1 and QE2V1.



Figure 2. Swelling percent of cryogels QE1V1 and QE1V2

As can be seen in the cryogels cross-linked at a rate of 1% have a higher swelling degree than 2% cross-linked, this is attributed, to that the latter have a higher rigidity to having a greater cross-linking, which limits their ability to swell.

C. Scanning Electron Microscopy.

In the micrographs obtained by the scanning electron microscopy, of the cross sections of the cryogels (Figure 3), one can see the formation of a macroporous structure.



Figure 3. Cross section. a) QE1V1, b) QE2V1, c) QE1V2, d) QE2V2



Figure 4. Longitudinal. a) QE1V1, b) QE2V1, c) QE1V2, d) QE2V2

Similarly, in the longitudinal sections observed the formation of microchannels (Figure 4), the low speed of immersion probably contributes to the formation of microchannels more defined, as can be seen by comparing the micrographs of the two speeds used for each level crosslinking.

On the other hand, the low speed contributes to an increase in the size of the macropores of cryogel (Figure 3), this is due to the time of formation of ice crystals is larger and therefore have more time to grow and have a structure more definite, that present is at higher speeds, where the ice crystals formed are smaller.

## D. FTIR spectroscopy.

To following shows the spectra of the synthesized cryogels's precursors, Q and E (Figure 5). As it can be apreciated in Q's spectra appear characteristic bands like 1577cm-1 which are atributed to the bending of the N-H group, 1341cm-1 bending vibration of the C-H links, 1052cm-1 vibration by voltage typical C-OH, 1659cm-1 vibration due to the tension of C = O, 2838cm-1 vibrations of tension C-H links, 3307 and 3379cm-1 flexural vibrations of N-H links. As for the spectrum of E,

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there are bands like 760cm -1 vibration by the deformation out of plane of C-H, 856 and 911cm-1 vibration that manifests the C-O links present in the strong ethers, 1097cm -1 typical vibration for tension C-C links, 1256cm-1 vibration by bending of C-H, 1460cm-1 vibration by deformation of the CH2 group, 1647cm-1 C-C bond vibration, 2875 and 3005cm-1 vibration by bending of C-H and 3527cm-1 vibration by tension of CH, among others [3][4].



Figure 5. IR spectra of Q and E

Figure 6. IR spectra of Q, E, QE1V2 and QE2V2

Figure 6 shows the spectra of the cryogels QE1V2 and QE2V2; along with the spectrum of Q and E; as can be seen the spectra of the cryogels continue to showing the main bands of the Q's spectrum, almost without modification. However, the observed changes are due to the influence of E in the crosslinking of the material. As expected, we observe that the higher the degree of crosslinking in the material, the influence of E is greater.

You can also note that for all materials shows the bending vibration of N-H, indicating that these groups are still present in the cryogels obtained; as well as an increase in the vibration by tension and bending of C-OH, which can be attributed to the breakdown of the E rings, observing this phenomenon more clearly in the spectrum of QE2V2, in the same way you can still identify the presence of typical group C-O of ethers, and the presence of the E chain.

## Conclusions

Was obtained a macroporous material which is stable and resistant in aqueous solutions, with a high degree of swelling, and it was found, that the shape and size of pores can be modified by changing the speed of immersion in their synthesis. The data obtained by FTIR spectroscopy test, shows that the cryogels obtained still have amino and hydroxyl groups in its structure, with which the cryogel may be able to interact and form complexes with metal ions.

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# POLYMERIC-BASED NANOHYBRIDS FOR COMBINED IMAGING AND THERAPY.

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Polymeric-based nanoshell particles constitute a special class of nanocomposite materials. They consist of concentric particles, in which particles of one material are coated with a thin layer of another one using different procedures [1]. Here, we present gold nanoshells formed by a PLGA core and an outer gold layer stabilized with PEG. The PLGA core is capable of carrying hydrophobic and hydrophilic drugs/molecules, whereas the gold shell can absorb light in the near infrared electromagnetic spectrum, conferring the platform the potential capability of combined imaging and chemical/photothermal therapies. As a proof of concept, PLGA nanoparticles were coloaded with the fluorescent dye indocyanine green (ICG) model drug and superparamagnetic Fe<sub>3</sub>O<sub>4</sub> NPs. In this manner, our platform should enable its simultaneous visualization by magnetic resonance (MRI) and NIR fluorescence imaging. The gold shell was grown by a seed-mediated approach to confer the platform the additional capability of photothermal therapy. Temperature increments of up to 15 °C in bulk solution were measured under short irradiation times at relatively low powers. Preliminary experiments in vitro indicate a good particle uptake by different cell lines. Also, a suitable biodistribution and an extensive residence in tumor site with a good fluorescent signal in in vivo animal models was observed even after 96 hour of injection through the mice tail vein by NIR fluorescence imaging.



Figure. a) TEM image sponge-like polymeric Au nanoshells. The inset shows the typical shape of viruses. b) Localization of the tumor by bioluminiscence. c) Fluorescence image showing the EPR retention of the nanoplatforms in the tumor site at 48 h post-injection.  $\lambda_{exc} = 710$  nm,  $\lambda_{em} = 840$  nm.

## ISOSORBIDE DERIVED MESOGENIC MONOMERS AND POLYMERS

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Isosorbide is a glucose based, chiral diol with complex stereochemistry. Owing to the unequal reactivity of the two pendent hydroxyl groups, one being endo and the other exo to the ring, it is an ideal candidate for the synthesis of asymmetric AB monomers. Isoidide, the isomer with both pendent hydroxyl groups exo to the ring, can be used as a building block for symmetric monomers. Mesogenic monomers have been synthesized by attaching one or more known mesogenic moieties to isosorbide or isoidide. Thermotropic polymers are known to have high melting point and liquid crystalline transition temperatures and high modulus and strength. However, some homo-polymers of mesogenic molecules tend to be intractable due to their melting point being higher than the decomposition temperature. Current approaches to make the LCP tractable include adding flexible spacers, disrupters, aliphatic chains and bulky side groups. Isosorbide derived mesogenic monomers have a built-in flexible spacer due to the bent shape of isosorbide disrupting the rigid rod like structure one would obtain by homo-polymerizing some of the known mesogens like naphthalene and biphenyl based monomers. The monomers are bulky and high melting, thus avoiding the issue of sublimation in condensation polymerization. Experiments are underway to synthesize polymers from these monomers, which are expected to retain mesogenicity while possessing a favorable processing window due to decrease in melting point and transition temperatures with respect to decomposition temperature.

**GENERAL TOPICS** 

## EFFICIENT SOLUTION OF THE FULL MOLECULAR WEIGHT DISTRIBUTION USING THE QSSA IN PRECISE POLYMER SYNTHESIS. APPLICATION TO NMP, RAFT AND ZIEGLER-NATTA POLYMERIZATIONS

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The modeling of the FMWD in addition polymerization is a challenging task, since it involves the solution of very large systems of ordinary differential equations (thousands to millions), usually exhibiting stiffness. Sophisticated numerical techniques have been implemented in a commercial package (Predici TM) in order to describe the full MWD, but for some mechanisms this tool has important limitations that will be discussed in this talk. We have recently developed a technique for the solution of the FMWD in which the equations are directly integrated by explicit algorithms after removing the stiffness of the system by application of the quasi steady state approximation (QSSA). In this paper, we illustrate the use of this technique by applying it first to nitroxide mediated polymerization and then to the more challenging RAFT system, which includes four polymer distributions. In this work the technique proposed is applied to different RAFT models concluding that, originating in the radical adduct population, the FMWD for the slow fragmentation theory shows a marked bimodality (not present under other theories) that has not been detected before due to limitations of the solution techniques used so far. To further show the potential of these techniques, its application to Ziegler Natta polymerization with a two-site catalyst is also discussed.

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# PREPARATION OF GRAFT MODIFIED MICROCRYSTALLINE CELLULOSE IN IONIC LIQUIDS

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Historically polymer science has focused on polymers derived from petroleum feedstocks. However, the most common macromolecule on earth, cellulose, is surprisingly under-utilized in polymer applications given its abundance and advantageous properties. Modification of natural polymers, such as cellulose, with synthetic polymers has excellent promise as an effective route to renewable, eco-friendly, biocompatible, biodegradable, and affordable alternatives to petroleum-derived analogs. One route to confer new chemical and physical properties to natural polymers involves grafting synthetic polymer chains onto natural polymers. Controlled/Living Radical Polymerization (C/LRP), has remarkable potential to prepare a wide array of functional materials through precise control of the polymer microstructure. Extending this chemistry to formulate cellulose-based synthetic hybrid copolymers, is a relatively unexplored field that could yield materials with new, practical properties and commercial application. For example, cellulose could be modified to yield paper-based membrane filters for desalinization, cellulose -based adsorbents for metals or oil recovery, or thermally-, pH- or concentration-responsive "smart" hybrid copolymers for a range of environmental applications.

Although cellulose does not readily dissolve in any common organic solvents, the ionic liquid 1ethyl-3-methylimidazolium acetate ([emim][OAc]) is a good solvent for cellulose, allowing graft modification with synthetic polymers in a homogeneous environment. We first functionalized microcrystalline cellulose with bromoester moieties, yielding a degree of substitution of ~1.5 (of the cellulose hydroxyl groups). PMMA chains were then grafted from the cellulose backbone using SET (Single Electron Transfer) polymerization. Size exclusion chromatography and NMR analyses established that graft copolymers were prepared. Subsequent acid hydrolysis of the ester linkages allowed determination of the molecular weight distribution of the grafted chains. The ratio of cellulose:PMMA, and therefore the extent of modification of the cellulose properties, can be readily controlled by varying the polymerization conditions.

# MANIPULATION OF POLYMER PROPERTIES BY SOLVENT CHOICE IN FREE-RADICAL ACRYLIC (CO)POLYMERIZATION

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Acrylic resins used as polymeric binders in automotive coatings are complex copolymers containing reactive functional (often hydroxyl) groups produced at high temperatures in a starved-feed semibatch process. Free radical copolymerization propagation kinetics of styrene (ST) with the hydroxyl-functional monomers 2-hydroxyethyl methacrylate (HEMA) and 2-hydroxyethyl acrylate (HEA), have been investigated systematically both in bulk and solution, using pulsed-laser polymerization (PLP) combined with size exclusion chromatography (SEC) and proton NMR. Monomer reactivity ratios and composition-averaged propagation rate coefficients in bulk are well represented by the implicit penultimate unit effect model [1]. It was found that solvent choice (n-butanol, toluene and DMF) has a significant effect on ST/HEMA copolymer composition, with a systematic variation in monomer reactivity ratios observed with solvent polarity. The rate effects are linked to corresponding solvent effects on homopropagation kinetics, and suggest that hydrogen bonding interactions need to be explicitly considered [2]. Solvent choice is shown to greatly affect polymer MW produced under semibatch operating conditions.

H-bonding has also been found to reduce the extent of intramolecular chain transfer to polymer (backbiting) reactions prevalent in acrylate systems. C13 NMR analysis indicates that negligible backbiting occurred during PLP of HEA, and H-bonding with solvent greatly reduces backbiting during butyl acrylate PLP experiments [3]. Use of alcohols as solvent increases molecular weight and reduces by a factor of five branching levels of poly(butyl acrylate) produced by semibatch operation [4], providing a novel method to synthesize materials with tailored microstructures.

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# KINETIC MODELING OF 1,3-DIENE POLYMERIZATION USING A NEODYMIUM-BASED CATALYTIC SYSTEM

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## Abstract

A mathematical model of the kinetics of 1,3-diene polymerization using a binary neodymium-based catalytic system has been proposed. A kind of lumping technique was used to describe the MWD in reasonably computing times without any assumption about the shape of the distribution. The model is able to fit experimental data for the evolution of molecular weight and polidispersity. The results of this preliminary simulation are used as a guide to design kinetics experiments that would lead to the improvement of the model and higher knowldege of the system under study.

## Introduction

Neodymium (Nd) based catalysts are highly effective for obtaining high-cis-1,4-polybutadiene [1]. An interesting and challenging aspect of this process is that polymerization is catalyzed by several active centers (ACs) whose difference between them is the number of alkyl substituents (up to 3). These ACs convert in each other with time by series (alkylation) reactions in the presence of organoaluminium compounds (OACs). Besides, each of them seems to propagate at different rate so that multimodal molecular weight distribution (MWDs) might be obtained [2].

On the other hand, in the field of polymerization process modelling, several simplified approaches and approximate numerical techniques have been extensively used to study the development of the MWD (see references in [5]). Very recently [6], it has been shown that direct integration of the equations (of the order of  $10^3$ - $10^6$ ) describing the full MWD in addition polymerization is feasible in reasonable computing times (less than an hour) using standard computers.

Notwithstanding the interest in the process under study, reports in the literature about mathematical modelling of the system under study are scarce [3, 4] and do not calculate the complete MWD but only estimates molecular weight averages by means of the moments method. Besides, those works consider only one type of AC.

In the present work, an alternative method for calculating the evolution of the complete MWD is proposed and applied to the modeling of 1,3-diene polymerization using a Nd-based catalytic system. It is considered that each AC leads to its own MWD. The distributions are treated as histograms and a set of ordinary differential equations describing the population of each bar is proposed. This kind of "lumping" technique allows one, in principle, to calculate multimodal MWDs by solving 10<sup>2</sup> ordinary differential equations (ODEs) without any assumption about their shape. Predictions of the models are compared against experimental results and similarities and differences between them are discussed.

# **Development of the model**

# Kinetic scheme and assumptions.

A simplified block diagram of the different steps involved in the process is shown in Figure 1. The details of the reactions that take place in every step are shown in table 1.



Figure 1. Steps involved in the process.

Table 1	. Kinetic	scheme	and rat	e exp	pressions	of the	chemical	reactions	considered.
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No.	Reaction name	Chemical equation	Rate expression
1a		$AlR_3 \rightarrow AlR_2Cl$	k <sub>A,0,3</sub> [NdCl <sub>3</sub> ][AIR <sub>3</sub> ]
1b		$NdCl_3 + AlR_2Cl \rightarrow AlRCl_2 \rightarrow NdRCl_2$	k <sub>A,0,2</sub> [NdCl <sub>3</sub> ][AIR <sub>2</sub> Cl]
1c		$AIRCl_2 \rightarrow AICl_3$	k <sub>A,0,1</sub> [NdCl <sub>3</sub> ][AIRCl <sub>2</sub> ]
1d	Formation of	$AlR_3 \rightarrow AlR_2Cl$	k <sub>A,1,3</sub> [NdRCl <sub>2</sub> ][AIR <sub>3</sub> ]
1e	ACS (NO	$NdRCl_2 + \langle AlR_2Cl \rightarrow AlRCl_2 \rangle \rightarrow NdR_2Cl$	k <sub>A,1,2</sub> [NdRCl <sub>2</sub> ][AIR <sub>2</sub> Cl]
1f	OAC)	$AIRCl_2 \rightarrow AICl_3$	k <sub>A,1,1</sub> [NdRCl <sub>2</sub> ][AIRCl <sub>2</sub> ]
1g	,	$AlR_3 \rightarrow AlR_2Cl$	k <sub>A,2,3</sub> [NdR <sub>2</sub> Cl][AlR <sub>3</sub> ]
1h		$NdR_2Cl + \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ $	k <sub>A,2,2</sub> [NdR <sub>2</sub> Cl][AlR <sub>2</sub> Cl]
1i		$AIRCl_2 \rightarrow AICl_3$	k <sub>A,2,1</sub> [NdR <sub>2</sub> Cl][AIRCl <sub>2</sub> ]
2a		$NdRCl_2 \rightarrow NdRCl_2M$	k <sub>i,1</sub> [NdRCl <sub>2</sub> ][M]
2b	Initiation	$NdR_2Cl \rightarrow HM \rightarrow NdR_2ClM$	k <sub>i,2</sub> [NdR <sub>2</sub> Cl][M]
2c		$NdR_3 \rightarrow NdR_3M$	k <sub>i,3</sub> [NdR <sub>3</sub> ][M]
3a		$NdRCl_2M_i \rightarrow NdRCl_2M_{i+1}$	k <sub>P,1</sub> [NdRCl₂MJ][M] <b>/∆J</b>
3b	Propagation	$NdR_2ClM_i \rightarrow MdR_2ClM_{i+1}$	k <sub>P2</sub> [NdR₂CIMJ][M]/∆J
3c		$NdR_3M_i \rightarrow NdR_3M_{i+1}$	k <sub>P,3</sub> [NdR <sub>3</sub> M <sub>J</sub> ][M]/ΔJ
4a	Chain transfor	$NdRCl_2M_i \rightarrow NdCl_2M$	k <sub>trM</sub> [NdRCl <sub>2</sub> M <sub>J</sub> ][M]
4b	to monomer	$NdR_2CIM_i \rightarrow MdRCIM \rightarrow RM_i$	k <sub>trM</sub> [NdR <sub>2</sub> CIM <sub>J</sub> ][M]
4c		$NdR_{3}M_{i} \qquad \longrightarrow NdR_{2}M \qquad \qquad$	k <sub>trM</sub> [NdR <sub>3</sub> M <sub>J</sub> ][M]
5a		$NdRCl_2M_i \rightarrow NdRCl_2$	k <sub>trOAC</sub> [NdRCl <sub>2</sub> M <sub>J</sub> ][AIR <sub>3</sub> ]
5b		$NdR_{2}ClM_{i} \rightarrow AlR_{3} \rightarrow NdR_{2}Cl \rightarrow + RM_{i}AlR_{2}$	ktroac[NdR2CIMJ][AIR3]
5c		$NdR_3M_i $ $\rightarrow NdR_3 $	k <sub>trOAC</sub> [NdR <sub>3</sub> M <sub>J</sub> ][AIR <sub>3</sub> ]
5d	Chain transfer	$NdRCl_2M_i \rightarrow NdRCl_2$	k <sub>trOAC</sub> [NdRCl <sub>2</sub> M <sub>J</sub> ][AIR <sub>2</sub> Cl]
5e	to OAC	$NdR_{2}ClM_{i} + AlR_{2}Cl \rightarrow NdR_{2}Cl + RM_{i}AlRCl$	k <sub>trOAC</sub> [NdR <sub>2</sub> CIM <sub>J</sub> ][AIR <sub>2</sub> CI]
5f		$NdR_{3}M_{i}  \int  \rightarrow NdR_{3}  \int$	k <sub>trOAC</sub> [NdR <sub>3</sub> M <sub>J</sub> ][AIR <sub>2</sub> CI]
5d		$NdRCl_2M_i \rightarrow NdRCl_2$	k <sub>trOAC</sub> [NdRCl <sub>2</sub> M <sub>J</sub> ][AIRCl <sub>2</sub> ]
5e		$NdR_2CIM_i \Rightarrow AIRCl_2 \rightarrow NdR_2Cl \Rightarrow + RM_JAICl_2$	k <sub>trOAC</sub> [NdR <sub>2</sub> CIM <sub>J</sub> ][AIRCl <sub>2</sub> ]
5f		$NdR_3M_i \rightarrow NdR_3$	k <sub>trOAC</sub> [NdR <sub>3</sub> M <sub>J</sub> ][AIRCI <sub>2</sub> ]
6a	Monomole-	$NdRCl_2M_i \rightarrow HNdCl_2$	k <sub>t</sub> [NdRCl <sub>2</sub> M <sub>J</sub> ]
6b	cular	$NdR_2CIM_i \rightarrow HNdRCl + RM_i$	kt[NdR2CIMJ]
6c	termination	$NdR_3M_i \rightarrow HNdR_2$	k <sub>t</sub> [NdR <sub>3</sub> M <sub>J</sub> ]
7a	Regenera-tion	HNdCl <sub>2</sub> $\rightarrow$ NdRCl <sub>2</sub>	ktrs[HNdCl2][M]
7b	of the active	HNdRCl $\rightarrow$ + M $\rightarrow$ NdR <sub>2</sub> Cl	k <sub>trS</sub> [HNdRCI][M]
7c	centers	$HNdR_2 \qquad \rightarrow NdR_3$	k <sub>trS</sub> [HNdR <sub>2</sub> ][M]

Reactions (1a)-(1i) are a set of serial-parallel reactions in which the Neodymium ACs are formed. In some recipes these reactions take place in a separate reactor and after a time known as "aging time" the catalyst mixture is added to the polymerization reactor. For the present work there is no aging time. This means that the raw materials (i.e.  $NdCl_3 \cdot 3L$  and  $AlR_3$ ; L=ligand) for the formation of ACs are added directly to the polymerization reactor so that such ACs are formed in

situ during all the course of the polymerization. It is important to mention that the NdCl molecules are in reality forming a complex with a ligand, although for reasons of space such ligand it is not explicitly indicated.

The initiation reactions (2a-2c) occur between the monomer and the mono-, di- and tri- alkylated Nd compounds formed through reactions (1a)-(1i). It is assumed that these species propagates with monomer (reactions 3a-5c) at different rates depending on the number of alkyl substituents. There is experimental evidence [2] supporting this assumption.

Chain transfer reactions occur by reaction of the propagating chain with monomer (reactions 4a-4c), with an OAC (reactions 5a-5f) or by a two-stage chain transfer (reactions 8 and 9).

## Mathematical model.

## Material Balances

The time evolution of the molar concentration (*C*) of a specie "i" in the reactor assuming this later is perfectly mixed is:

$$V\frac{dC_i}{dt} = -C_i\frac{dV}{dt} + (C_i)_{in}Q_{in} - C_iQ_{out} + r_iV$$
<sup>(1)</sup>

*V* is the reactor volume;  $Q_{in}$  and  $Q_{out}$  are volumetric inflow and outflow streams, respectively. The molar concentration of the specie "*i*" in the feed stream is  $(C_i)_{in}$ . For batch reactors, as in the present case of study, the inflow and outflow terms (second and third terms of the right-hand side) are zero. The net rate of consumption/production of the species "*i*" by chemical reaction is represented by  $r_i$ , which is equal to the summation of the rate expressions of the chemical reactions shown in Table 1 where the "*i*" species participates. As it is conventionally done, a given rate expression is affected by the minus sign for consumption and by the plus sign for production. The way in which  $r_i$  is calculated for the "live" and "dead" chains is explained in the following section.

## Molecular weight distribution (MWD)

*MWD* is considered as a histogram constituted by *NB* boxes of class width  $\Delta J$ , where *J* is the degree of polimerization (d.o.p.) (see Figure 2).  $J_i$  is the representative d.o.p. of the *ith* box, this is,  $J_i$  is the class mark. Thus, the rate expressions for reactions (3a)-(3c) shown in table 1 represent the rate at which the population of a box *i* moves to the box *i*+1.



The propagation rate equation of a growing chain gives us the number of monomer molecules that are being added to the chain per unit time. If  $\Delta J$  is divided by this rate then the time required for a chain to pass

**Figure 2.** Schematic description of the histogram for calculating the MWD.

from the box i to the box i+1 is obtained. The inverse of this quantity multiplied by concentration of growing chains in the *i*th box gives the rate  $r_{g,i}$  at which the population of such box moves to the *i*th+1 box:

$$r_{g,i} = k_p \left[ IM_i \right] M \left[ \Delta J \right]$$
(2)

Where [M] and  $[IM_i]$  are the molar concentrations of monomer and growing chains, respectively.  $IM_i$  represents NdRCl<sub>2</sub> $M_i$ , NdRCl $M_i$ , or NdR<sub>2</sub> $M_i$ . Then, the MWD is given by

$$\left[IM_{i}\right] = \sum_{i=1}^{NB} \left( \left[NdRClM_{i}\right] + \left[NdR_{2}ClM_{i}\right] + \left[NdR_{3}ClM_{i}\right] \right)$$
(3)

### Implementation

It is assumed that the maximum attainable d.o.p. is  $1 \times 10^5$  and that NB=100, hence  $\Delta J=1 \times 10^3$ . The number ordinary differential equations (ODEs) solved were 214, from which 100 ODEs correspond to the MWD of live chains, 100 of dead chains, 13 for the non-polymeric chemical species shown in Table 1, and 1 ODE that accounts for the volume contraction of the system because of the density difference between monomer and polymer. The set of ODEs were solved by the Runge-Kutta method with adjustable step size in about 3 minutes on a PC.

### **Results and Discussions**

Model's prediction for the evolution of the number-average (Mn) and weight-average (Mw) molecular weights are compared with experimental data [4] in Figure 3 (left), as well as the correspondent theoretical and experimental polidispersity evolutions (PDI=Mw/Mn) (Figure 3, right). As it can be observed, model's prediction reasonably agrees with the experimental data. The final MWD predicted by the model is shown in Figure 4, where each point corresponds to the population of the bars. It is evident that the number of bars as well as the lumping technique

employed are adequate to describe with enough detail the MWD.



**Figure 3.** Comparison of model's prediction (lines) against experimental data (symbols). Left: number-average (Mn) and weight-average (Mw) molecular weights. Right: Polidispersity.





Figure 5. Concentration of the different active

In Figure 5 the concentrations of ACs as a function of conversion are shown. The concentration of the di-alkylated specie is the highest because it is inactive in polymerization [7]. Thus, only the mono-alkylated y tri-alkylated species form polymer chains which tend to form different molecular weights because their value of  $k_p$  is different in at least one order of magnitude. At low conversion, let say <0.2, the concentration of mono-alkylated AC is larger than the one of trialkylated so that the rate of polymerization  $(R_p)$  and the molecular weight are lower compared to that obtained at intermediate and high conversions where the concentration of tri-akylated AC is higher. Therefore, this preliminary simulation suggests that valuable kinetic information (e.g.  $k_{\rm p}$ for each AC) can be obtained from experimental data by analyzing kinetic information at extreme conversions. It also suggest that another way to contrast the kinetic behaviour of the mono- and try-alkylated ACs is to perform polymerizations using catalyst mixture of very contrasting aging times (for vey long aging times a much higher concentration of the trialkylated specie is expected). As more independent experimental information becomes available it will be feasible to reduce the number of unknown kinetic parameters. In this direction it would be very useful to known the kinetics of alkylation of the neodymium species. These experiments would be helpful to confirm/refute the model assumptions and to increase the degree of validity of the model.

### Conclusions

The preliminary simulation shown in this work indicates that the mathematical model proposed is able to reasonably adjust to important features of a 1,3-butadiene polymerization using a binary neodymium-based catalytic system. This model can be used as a guide to design kinetic experiments in order to test the model assumptions as well as to estimate kinetic

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# IS IT CORRECT TO MODEL THE RAFT POLYMERIZATION USING THE PREDICI SOFTWARE PACKAGE?

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Recently, we reported the implementation of a new numerical methodology to solve for the fullmolecular weight distribution (full-MWD) models of some addition polymerizations, like free radicals and nitroxide mediated polymerization. [1] The reversible addition-fragmentation chain transfer (RAFT) is one of the most studied processes in the addition polymerization in the last decade. However, to model the full-MWD in RAFT process is a difficult task because the reaction mechanism involves four polymer distributions. In addition, the distribution of adducts species is a 2-dimensional distribution, which increases the mathematical complexity of the model.

RAFT polymerization still poses fundamental kinetic questions related to key mechanistic steps. Different theories have attempted to explain the rate retardation in reactions mediated by certain RAFT agents, but very few papers have described the FMWD in RAFT systems, despite the fact that simulation studies of the MWD could help in model discrimination. In this work the technique proposed is applied to different RAFT models concluding that, originating in the radical adduct population, the FMWD for the slow fragmentation theory shows a marked bimodality (not present under other theories) that has not been detected before due to limitations of the solution techniques used so far, especially Predici commercial software. [2]

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# CHANGES ON MOLECULAR WEIGHT DISTRIBUTION AND MECHANOSTATICAL PROPERTIES PRODUCED ON PLASTICIZED PVC FORMULATIONS DEGRADED ISOTHERMICALLY AT DIFFERENT TEMPERATURES OR, AT ENVIROMENTAL CONDITIONS

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### Abstract

PVC is generally degraded during processing, producing several undesirable effects. In this work, mixtures of calcium and/or zinc stearates and epoxidized soybean oil are used as stabilizers. The formulation composition was systematically varied considering the following parameters: a) presence of epoxidized soybean oil, b) the  $CaSt_2/ZnSt_2$  ratio. Each formulation underwent the following degradation conditions: a) isothermal heating (IH) at 60°C, b) IH at 120°C, c) IH at 150°C and, d) environmental outdoor conditions. Thermal stability was followed during isothermal heating by determining: a) the molecular weight distribution and, b) the changes in the tensile properties.

### Introduction

The PVC formulations usually are degraded during processing, producing an undesirable HCl release, generating polyene sequences in polymer chains, producing discoloration in the material and, modifying its mechanical performance [1]. Besides, the polyene sequences may react to form branched polymer chains, as well as low molecular weight molecules [1]. The accelerated degradation studies have been commonly used [2], however, it has not been demonstrated that, in all cases, the observed trends at high temperatures can be directly extrapolated to the service conditions. Therefore, it is useful to carry out degradation studies at different temperature to estimate the degrading behavior at environmental conditions. Due to its technological relevance, the mechanostatical changes produced by the degradation process in several plasticized PVC formulations were followed. The plasticized PVC formulations (45 phr di(ethyl hexyl) phthalate -DEHP- and, 0 or 6 phr of epoxidized soybean oil -ESO-) were stabilized with calcium and/or zinc stearates (CaSt<sub>2</sub>./ZnSt<sub>2</sub>). The formulations underwent the following degradation conditions: a) isothermal heating (IH) a 60°C, b) IH at 120°C, c) IH at 150°C and, d) environmental outdoor conditions. Besides, to explain, at least partially, the origin of the produced mechanical changes, the molecular weight distribution of the soluble fraction was additionally measured. Finally, this work results were correlated with the polyene accumulation behavior of the same formulations determined for a parallel work [3].

## **Experimental**

## **Preparation and post-proccesing**

The samples to be post-processed were prepared as follows: (a) dry blending the components, (b) pelletizing the dry-blend (twin-screw extruder Leistritz 276L/32D) and, (c) extruding the pellets (to obtain ribbons). Two different DEHP/ESO ratios were used: 45/0 or 45/6 (phr/phr). For each

one of the DEHP/ESO ratios, the following  $CaSt_2/ZnSt_2$  ratios (phr/phr) were used: 0.0/1.0, 0.2/0.8, 0.4/0.6, 0.6/0.4, 0.8/0.2 and, 1.0/0.0; in all formulations, the total content of stearates was 1.0 phr. The samples were post-processed by heating at 60, 120 and 150°C, using a force convection oven (FRELAB); the maximum degradation times ( $t_{max}$ ) were, respectively, 44 days, 12 h and 3 h. Other post-processing procedure was carried out by exposition at environmental outdoor conditions; in this case,  $t_{max}$ =182 days.

## Characterization

The changes on the stress-strain behavior of degraded samples (ASTM D638 type II specimens) were determined using a Universal Testing Machine from United (SFM10), characterizing the samples at room temperature and with a cross-head speed of 50 mm/min. The molecular weight distribution was determined by gel permeation chromatography (Waters Model 2414).

## **Results and Discussions**

By space restrictions, in this paper will be only presented and briefly discussed some relevant results. In Figure 1 is presented the normalized modulus ( $E^*= 100 E(t)/E(0)$ ) as a function of scaled time ( $tf_T$  or  $tF_T$ ) for formulations containing more ZnSt<sub>2</sub> than CaSt<sub>2</sub>. There, it can be noticed that, the temperature effect on the degrading behavior of formulations without ESO (left column) can be scaled by using the thermal accelerating factors indicated in figure ( $f_{TS}$ ). However, such effect can not be adequately scaled on formulations containing ESO. Therefore, in such figure, arbitrary factors (F<sub>T</sub>s) were used in order to be able to plot all the data in the same graph. In case of formulations lacking of ESO, the factors  $f_{120}$  are practically independent on the relative content of CaSt<sub>2</sub> (their values are ~400). However, the factor  $f_{150}$  for formulation lacking of CaSt<sub>2</sub> ( $f_{150}$ =2150) is clearly higher than the ones corresponding to formulations containing such stearate (such values are very similar between them; ~1400). Regarding the MWDs presented in Figure 2, it can be noticed that, at 150°C, when the  $X_{CaSt2}=0.6$  a clear domain of the chain scission process occurred. Nevertheless, at the higher CaSt<sub>2</sub> contents, there is a very slight tendency to shift the MWD curve towards the right side; the largest change in observed on the low molecular weight zone. With respect the results for samples degraded at 120°C, an important displacement of their MWD curves towards the left side can be appreciated in Figure 2, denoting a clear domain of chain scission reactions. Analyzing the degrading behavior of samples heated at 60°C, it can be observed in Figure 2 that, such degrading process does not produced significant changes on MWDs of the respective samples. Finally, the environmental outdoor degrading process produced on samples, the highest occurrence of chain scission reactions, producing the largest shift of the MWD curves towards the left side. Due to the normalize ultimate properties ( $\sigma^{*}=100 \text{ s(t)/s(0)}$  and,  $\epsilon^{*}=100$ e(t)/e(0)) show a linear dependence with the degradation time, in Table 1 are present the corresponding  $d\sigma^*/dt$  and  $d\epsilon^*/dt$  values. Considering the experimental errors involved in such derivatives, the changes on ultimate properties that fulfill some of the below presented conditions will be considered as non-significant statistically; such conditions are: a) for outdoor conditions,  $|dj^*/dt| \le 3x10^{-3}$  %/h, b) for 120°C,  $|dj^*/dt| \le 1.3$  %/h and, c) for 150°C,  $|dj^*/dt| \le 5$  %/h (j\*:  $\sigma^*$  or  $\varepsilon^*$ ). Analyzing the results for environmental degradation process, it can in general terms be noticed that, in the formulations containing ESO, the degradation produced very slight decrements on the  $\sigma^*$  values, but considerable diminutions on the  $\epsilon^*$  values. Otherwise, the lacking of ESO samples degraded in an equivalent way, underwent important decrements on the  $\sigma^*$  values and catastrophic decrements on the  $\varepsilon^*$  values, demonstrating the beneficial effect of the ESO presence. In general terms, the formulations 45/6 degraded at high temperatures (120°C or, 150°C), maintained during the test practically unaltered their ultimate properties. Regarding of the changes on  $\sigma^*$  produced on





indicated con	ditions.					
c		<sup>•</sup> /dt, %/h		dε*/dt, %/h		
X <sub>CaSt2</sub>	Outdoor conditions	120ºC	150ºC	Outdoor conditions	120ºC	150⁰C
		D	EHP/ESO (	phr/phr): 45/0		
0.0	-8 E-03	1.9	-0.5	-19 E-03	-2.8	-19.0
0.2	-9 E-03	2.7	2.1	-24 E-03	0.2	-9.3
0.4	-8 E-03	1.5	-0.5	-20 E-03	-0.6	-9.5
0.6	-11 E-03	1.4	1.0	-23 E-03	-0.5	-3.7
0.8	-10 E-03	2.0	1.2	-20 E-03	-0.5	-4.8
1.0	-8 E-03	0.8	1.1	-19 E-03	-0.1	-4.1
	DEHP/ESO (phr/phr): 45/6					
0.0	-3 E-03	0.4	-0.3	-8 E-03	0.1	-6.1
0.2	-1 E-03	-0.1	-1.9	-7 E-03	0.3	-5.9
0.4	-5 E-03	0.0	-2.0	-11 E-03	0.4	-5.9
0.6	-0 E-03	0.6	0.7	-6 E-03	0.5	-2.0
0.8	-4 E-03	0.2	0.3	-16 E-03	0.5	-2.7
1.0	-5 E-03	0.9	2.2	-11 E-03	0.1	-3.1

Tabla 1. Modification rate of normalized ultimate properties for indicated formulations, degraded at indicated conditions.

samples 45/0, it is remarkable that, while the modifications produced at 150°C are almost negligible, at 120°C, important increments on the  $\sigma^*$  values were produced during the test. Finally, the heating at 150°C produced on such samples, important decrements on the  $\epsilon^*$  values (especially in the formulation lacking of CaSt<sub>2</sub>). Conversely, at 120°C, excepting the formulation lacking of CaSt<sub>2</sub> (which decreased catastrophically its elongation), the other formulations 45/0 maintained practically unaltered their  $\epsilon^*$  values.

# Conclusions

The behavior of a set of formulations that underwent different degrading process were presented, demonstrating that, the trends observed at a given degradation temperature, usually can not be extrapolated to another temperature. Besides, as expected, the samples degraded at environmental conditions, in some cases exhibited distinctive behaviors as compared with isothermal degradation conditions; such characteristic avoid propose adequate scaling factors, to allow apply trends observed on accelerated experiments, to predict the behavior at wearing conditions.

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# DEEP EUTECTIC SOLVENTS ASSISTED SYNTHESIS OF FUNCTIONAL MATERIALS

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FP is a self sustained polymerization reaction where initiation (either thermal or light induced) is triggered at one of the ends of the reactor, typically a long tube. Thus, a well-defined polymerization front propagates axially along the reaction vessel (from one end of the reactor to the other) taking advantage of the exothermic nature of acrylic polymerizations. Deep Eutectic Solvents (DESs) are a type of ionic liquid that contain uncharged counterparts besides anions and cations, which form a eutectic.

DESs based upon mixtures of Acrylic Acid (AA) or Methacrylic Acid (MAA) and Choline Chloride (CCl) demonstrated superior performance than regular organic solvents and even ionic liquids for frontal polymerizations (FPs). The use of different pairs of compounds (e.g. AA : CCl or MAA : CCl) mixed in different molar ratios (e.g. 1.6 : 1 or 2 : 1, respectively) allowed the preparation of tailor-made DES. Tailored viscosities offered the possibility of controlling the front temperature and velocity (by minimizing convection instabilities that can eventually result in front collapse) and thus, enhanced polymer conversion (up to ca. 75% and 85% in AA-CCl DES and MAA-CCl DES respectively). The use of DES also favored the easy tuning of the ratio of double bonds per molecular weight to a certain threshold value that, in IL has been reported to be crucial for preserving the self-propagating nature of FP. Besides these interesting features, the possibility of CCl recovering and reutilization in subsequent FPs emphasized the "green" character of the use of DES monomers in FPs. This work broadens the scope of the FP technique in a way that is beneficial in the polymers and gels field, especially potentially in the biocompatible gels field.

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# LOW-FIELD NMR APPLIED TO THE STUDY OF POLYURETHANES IN BULK

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Low-field NMR is a powerful tool for the characterization of chain motion in entangled polymer melts, polymer networks and related mobile polymeric systems [1]. An important feature of the dynamics of cross-linked or entangled chains is the semi-local anisotropy. Fast motions such as Rouse modes are ultimately hindered by the presence of topological restrictions. In addition, those constrains also have a deep influence on the cooperative dynamics, i.e. chain reptation. In consequence, long-lived orientation correlations are induced. Their magnitude, which is related with the NMR-observable [2], is directly linked to microscopic parameters such as the crosslink density or the entanglement length.

With this tool a significant insight can also be gained for systems that undergo a transformation from one limit to the other, i.e., to linear polymers undergoing cross-linking [3], gelation [4] or crystalisation [5].

In the present communication we will describe the application of this technique to the study of the kinetics of polymerization of polyurethanes in bulk. We followed the polymerisation reaction in the preparation of prepolymers, isocyanate- and hydroxyl-terminated, checking the effect of the end group. Formulations of different types of polyurethanes, thermoplastic and thermosets, soft and rigid, etc., were prepared, and their kinetics in bulk followed. Results were compared with those obtained by FT-IR.

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### Squeeze flow film of a yield stress liquid

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### MEXICO

### Abstract

Theory and experiments are described in which a biological fluid was squeezed between two parallel glass plates of separation by a constant force F applied at time t = 0. The yield stress phenomenon occurs when the force becomes independent of the Weissenberg number and the system behaves as a solid. However, when the force overcomes the critical point (yield stress), the material begins to flow (moderate and high Weissemberg number). This behavior depends on the structural, kinetics and the viscoelastic fluid properties which are analyzed here through dimensionless parameters associated to each mechanism. To zeroth order, analytical-numerical expressions were found that relates the axial force measured in one of the plates to the viscosity of the fluid. Finally, theoretical results are predicted using rheometric data for an aqueous wormlike micellar solution of cetyl trimethyl ammonium tosilate (CTAT) at different concentrations.

### **1. INTRODUCTION**

In recent years the attention has been devoted to the problem of a non- Newtonian liquid being squeezed between two circular surfaces. This so-called squeeze film problem has a particular relevance in lubrication and it is interest to assess the usefulness of lubricants with non-Newtonian oils with the same viscosity al small rates of shear. The squeeze film facilitates this assessment by allowing us to measure the effect of elastic properties on the load bearing of non-Newtonian liquids. The evidence presented so has often been contradictory. Theoretical studies such as those commented that since theoretical analyses seem to be at variance with experimental evidence there is a need for more detailed theoretical studies involving more general equation of state (N. Phan-Thien, 1984). Complex fluids have also been used in enhanced oil recovery operations, especially those related with fracturing of subterranean functions. The extraction of additional amounts of oil can be achieved by hydraulically inducing fractures in the rock formations. Water-based fracturing fluids have been dominated by the use of high molecular weight water-soluble polymers. Recently, polymer-free fracturing fluids, based on viscoelastic surfactants have been Developer for fracturing underground formations. Fluids made of viscoelastic surfactants can provide improved fracture conductivity in comparison to polymerbased fluids. Viscoelastic surfactants are characterized by entangled network of large worm-like Michelle structures. These structures break and reform during flow, exhibiting variable and rich rheological behaviour of viscoleastic surfactants by constitutive equations has been a challenge issue. These systems exhibit Maxwell-type behaviour in small-amplitude oscillatory shear flow and saturation of the shear stress in steady simple shear, which leads to shear banding flow. Hydraulic fractures are characterized by having one dimension, the width, very small compared to the lateral dimensions, height and length (Soltero et al., 1999). This is the geometrical characteristic of the lubrications approximation, which assumes that the flow is well approximated by a locally uniform flow between parallel plates separated by the local fracture width. Lubrication theories have been applied to squeeze films using Oldroyd-B type constitutive equations [1-6]. In view of the important technological applications, it is surprising that the

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rheological modelling of viscoelastic surfactants (or wormlike micellar systems) in lubrication squeeze films has not been given much attention in the current literature. This is the subject of the present theoretical investigation. Worm like micellar systems subjected to non-linear shear flows within the non-linear regime of deformations have been analysed with an Oldroyd-B equation coupled to a time-dependent equation for the structure. The evolution equation for structural changes was conceived to account for the kinetic process of breakage and reformation of the micelles under flow. This constitutive equation has been shown to predict shear and oscillatory data of wormlike solutions very well (Manero et al., 2002; Soltero et al 1999)

### 2. PROBLEM FORMULATION

We considered cylindrical polar coordinates  $(R,\Theta,Z)$ , the axis being alone the normal axis to the plates, such that the lower and upper plates are given by Z = 0 and Z = h(t), respectively. Both plates are assumed to be a radius a. The components of the velocity vector in the  $(R,\Theta,Z)$ direction are denoted by  $V_R, V_{\Theta}$  and  $V_Z$ , respectively. Since h(t) is very much smaller than a, i.e h(t)<<a, it is customary to apply the lubrication approximation to squeeze film flow, which essentially involves the neglect of the inertial terms in the stress equations of motion and the application of an ording process to the remainder of the terms in the governing equations. The boundary conditions are:

$$V_{(R)} = 0, \qquad V_{(Z)} = 0, \qquad \text{on} \qquad Z = 0$$
 (1)

$$V_{(R)} = 0$$
  $V_{Z} = h(t)$  on  $Z = h(t)$  (2)

### **3. MOMENTUM AND MASS EQUATIONS**

The momentum and the mass conservation are given by the following non-linear partial differential equation:

$$0 = \nabla \cdot \mathbf{T} + \rho \mathbf{g} \tag{3}$$

$$\nabla \cdot \mathbf{V} = 0 \tag{4}$$

In equations (3-4) has been used the fact that the inertial mechanism are small and the complex liquid does not changes its volume (incompressible liquid).

### **3.1 CONSTITUTIVE EQUATION BMP**

In order to characterize our system (micellar aqueous solution) is proposed the BMP model (equation 5-6). These equations are a set of non-linear partial differential equation that couples the codeformational Maxwell equation with kinetic equation. This Kinetic equation, was conceived to taking account the evolution of the transient structure due to two principal mechanism. The first mechanism is relationship with the structural processes and the second one

to the work done to break-down the structure. In equation (5)  $\sigma$  is a viscoelastic stress,  $\sigma$  is the upper-convected derivative of the stress tensor,  $\eta$  is the viscosity function, D is the rate of

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deformation tensor,  $II_D$  is the second invariant of D and  $G_0$  is the elastic modulus. In equation (6)  $\eta_0$ ,  $\eta_\infty$  are the viscosities at zero and very high shear rates, respectively,  $\lambda$  is the structural relaxation time and k can be interpreted as a kinetic constant for the structure breakdown, all five parameters of the model  $(\eta_0, \eta_\infty, G_0, \lambda, k)$  are related to the fluid properties and can be estimated from independent rheological experiments in steady and unsteady flows (Manero. O et al., 2002).

$$T=-pI+\sigma$$
(5)

$$\sigma + \frac{\eta(II_{\rm D})}{G_0} \overset{\nabla}{\sigma} = 2\eta(II_{\rm D})D$$
(6)

$$\frac{d}{dt}Ln\eta(II_{D})^{\lambda} = 1 - \frac{\eta(II_{D})}{\eta_{0}} + k\lambda \left(1 - \frac{\eta(II_{D})}{\eta_{\infty}}\right) \sigma: D$$
(7)

### 4. DIMENIONLESS VARIABLES

In order to simplify the momentum and rheological equations, the next dimensionless variables are proposed:

$$z = \frac{Z}{h(t)}; r = \frac{R}{a}; v = \frac{V_{(R)}h(t)}{\frac{\Box}{ah(t)}}; w = \frac{V_{(Z)}}{\frac{\Box}{h(t)}}; \tau_{(ik)} = \frac{\sigma_{(ik)}}{G_0}; p = \frac{h^3 P}{a^2 \eta_0 h(t)}$$
(8)

Where h(t) is the gap of the plates, a is the radius of the pipe,  $G_0$  is the elastic module,  $\eta_0$  is the viscosity to low shear rate res and  $\stackrel{\square}{h}(t)$  is the time derivative of h(t).

### 5. DIMENSIONLESS NUMBERS

Using (8), the non-dimensionless components of the momentum, continuity and constitutive equations and the normal force are obtained. In addition, the following non-dimensional groups are defined:

$$\alpha = \frac{h}{a}; \quad We = \lambda_0 \frac{\langle V \rangle}{h}; \quad A = \left(\frac{\lambda}{\lambda_0}\right) \quad B = \left(\frac{\lambda}{\lambda_\infty}\right); \quad C = \left(AB\right)^{1/2} = \frac{\lambda}{\lambda_G} = \frac{\lambda}{\sqrt{\lambda_0 \lambda_\infty}}$$
(9)

Where the characteristic velocity is given by the next relationship  $\langle V \rangle = \frac{ah}{2h}$ . The first group is a ratio of two characteristic longitudes, the axial and radial longitude. It is important to note that  $\alpha$  is less than the unit, for this reason,  $\alpha$  is the perturbation parameter [1-3]. The second group is the Weissenberg number (*We*), which represents the product between one characteristic time

(Maxwell relaxation time which is associated to the viscoelastic properties of the fluid  $\lambda_0 = \eta_0 G_0^{-1}$ ) and the characteristic shear-strain X When  $We \ll 1$ , the viscous process are dominant over the elastic component. On the other hand, when  $We \gg 1$ , the opposite behaviour is clearly seen. The third group is a ratio between two characteristic times, one of them associated to the structural

process and the other one, to the viscoelastic properties. When the Maxwell time is larger  $(\lambda_0 = \eta_0 G_0^{-1})$  than the structure time and the fluid structure recovers faster than it destroyed by flow. Bautista et al. (1999) showed that when the structural time  $\lambda$  is larger than the Maxwell time, the form of the thixotropics loops and shape are predicted, since the structure of the fluid does not recover during the deformation period, i.e. destruction of the structure is faster than recovery. The fourth group (B) is the ratio of the viscosities at low and high shear rates. This group is a measure of the shear-thinning (B > 1) and shear-thickening (B < 1) behavior. Finally the last group is a product of the dimensionless numbers A and B. This group can be interpreted as the square ratio of two geometrical mean relaxation times, (defined as  $\lambda_0 = \eta_0 G_0^{-1}$ ,  $\lambda_{\infty} = \eta_{\infty} G_0^{-1}$ ),

so the dimensionless number C can be rewritten as  $C = \sqrt{AB} = \frac{\lambda_0}{\lambda_G} = \frac{\lambda_0}{\sqrt{\lambda \lambda_\infty}}$ . The time  $\lambda_G$  is related

to the structural and high shear-rate characteristic times.

### 6. RESULTS AND DISCUSSION

In order to resolve the set of dimensionless equations, it is seek a perturbation solution in terms of the small parameter  $\alpha$  for the axial and radial velocities, pressure gradient and shear stress. Finally, neglecting inertial and normal stress mechanisms, the normal force is given by the following integral expressions

$$F_{z} / F_{N} = -\frac{2}{3} \int_{0}^{1} W e^{-1} \tau_{(rz)0}(X_{1}) r^{2} dr$$
(10)

In equation (9)  $We^{-1}$  and  $X_1$  is the Weissemberg number and the shear starin to zero order in the perturbation parameter respectively. The viscous force is a function of the structural, viscous and structural mechanisms and the velocity of the top disc.



Figure 1. Force to zeroth order versus Weissenberg number for different value of the dimensionless groups.

In Figures 1-3 the non dimensional force is plotted versus Weissenberg number for differ4ents value of the dimensionless number A. It is clear that the squeeze flow, to zero order reproduce the viscosity curve for different vale of the parameters A, which is a measure of the shear-thinning or shear thickening in the system [1].



Figure 2. Force to zeroth order versus Weissenberg number for different value of the dimensionless groups.



**Figure 3.** Force to zeroth order versus Weissenberg number for different value of the structural relaxation time. Inset the the apparent yield stress vs Weissenberg number as a function of the structural relaxation time

## 7. CONCLUSIONS

To sum up, we have developed a perturbation solution to a continuous-flow squeeze film of non-Newtonian fluids. This simulated the flow in a conventional squeeze film by continuously injecting fluid in to the narrow gap between two circular plates through the lower plate. The liquid is characterized with a model that couples the Upper-Convective Maxwell equation and kinetic equation that accounts for the structural changes induced by the flow. The model employs five parameters can be obtained from independent rheological experiments, and then they can be used to predict other rheological data. The study points to the following conclusions.

1. Clearly  $F_{00}/F_N$  is a measure of the viscous effects and is the largest contribution to load bearing. Its magnitude almost exactly parallels the variation in viscosity with rate of shear.

$$\overline{F}_{0,m} = -\frac{2}{3} \int_{0}^{1} \tau_{(rz)0}(X_1) r^2 dr$$
(11)

2.- Similar conclusions have arrived others authors for the flow of non-Newtonian liquids in a conventional squeeze film whom the lubrication approximation is used and h(t) is replace by a  $\dot{h(t)} = \frac{\langle V \rangle a}{2h}$ , being the constant approach velocity of the disc in the conventional squeeze film.

3. Normal-stress or elastic effects are represented by the term  $F_{12}$ . Figure (8) shows that  $F_{12}/F_N$  is negative for small We and for critic Weissenberg number becomes positive and can increase very rapidly. This demonstrates that although the overall effect is small and negative for small we it is possible for normal stress effects to.

4. All physical mechanism, are given by the set of dimensionless groups.

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# POLYVINYL ACETATE NANOGELS BY MICROEMULSION POLYMERIZATION AND CROSSLINKED BY GAMMA AND UV RADIATION

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Poly(vinylacetate) nanolatices (PVAc) synthesized by microemulsion polymerization were crosslinked by both gamma and UV radiation. PVAc colloidal nanolatices before irradiation had particles with average diameter (Dp) of 58 nm, 10 % of polymer content and weight average molecular weight (Mw) of 562,000 g/mol. PVAc nanolatices irradiated by gamma radiation in a range from 1 to 13 kGy in air at room temperature showed high degree of crosslinking without use of crosslinking agent while those irradiated by UV radiation were crosslinked in the presence of divinylbenzene (DVB) and allyl methacrylate (AMA) at short irradiation times (from 30 to 300 seconds). Gel/sol analyses in both cases showed high yield of crosslinking (high gel content). Infrared spectroscopy (FTIR) studies did not show degradation of irradiated PVAc nanolatices. Dp's of the irradiated nanolatices were < 100 nm. Finally, PVAc irradiated samples were characterized by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Higher degradation temperatures were found for crosslinked PVAc: 10 % weight losses were 261 °C for uncrosslinked PVAc and 320 °C and 313 °C for UV and gamma rays crosslinked PVAc. Glass transition temperatures increased from 28 °C for PVAc, to 42 °C and 39 °C for UV and gamma rays crosslinked PVAc, respectively.

# HIGH SWELLING HYDROGELS OF POLY(ACRYLAMIDE-CO-ACRYLIC ACID) CHARACTERIZED BY RAMAN SPECTROSCOPY

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## Abstract

Therefore, in the literature, they are also classified within the expandable polymer networks. The features of monomers that form the hydrogels and the degree of crosslinking, determine the swelling properties of the dry hydrogel (xerogel) and their applications. In this work, hydrogels were synthesized by copolymerization of acrylamide (AAM) and acrylic acid (AAc), using 2,2-azobis(2-amidinopropane) hydrochloride (V-50) as initiator and N, N'-methylenebisacrylamide (NMBAM) as crosslinking agent. The effects of AAm/AAc ratio and the amount of crosslinking agent on the swelling properties of hydrogels were studied. The presence of AAm and AAc units in the hydrogels was confirmed by Raman spectroscopy analyzing the signals corresponding to 3064 and 3394 cm<sup>-1</sup> (NH<sub>2</sub>), 476 cm<sup>-1</sup> (O-C-N) of (AAm units) and 1984 cm<sup>-1</sup> (AAc units), confirming the existence of such units in the hydrogels. Absorption studies of pure water were carried out at room temperature, observing that swelling degree increases with AAc concentration and decreases with the percentage of MBAAm. The synthesized hydrogels in a 60/40 ratio of AAm/AAc showed the higher swelling degree.

## Introduction

Hydrogels are a group of (co)polymers with cross-linked networks. Their structures are heterogeneous in different orders in micro-morphology [1]. Many methods are available to prepare hydrogel materials. They are mainly made from water-soluble monomers by radical polymerization reactions. The most popular water-soluble monomers include acrylic acid, acrylamide and their derivatives. These monomers can be used to synthesize cross-linked homopolymers and copolymers consisting of different comonomers by aqueous solution or other polymerization processes. Another way to synthesize hydrogel materials is to prepare interpenetrating polymer network (IPN) composites from water-soluble monomers with other materials. In addition, some natural materials (e.g., chitosan) are also used as hydrogels.

One of the most important applications of hydrogel materials is to bind and capture metal ions (especially heavy metal ions) from water. [2] found that polyelectrolyte binds metal ions in three ways: 1) Cooperative and stoichiometric. 2) Non-cooperative and stoichiometric, and 3) Cooperative and non-stoichiometric. The mechanism of metal ion adsorption is determined by the three-dimensional chemical structure of the ligand, hydrophobicity and the charge density of the polyelectrolyte [1].

Heavy metal ions are harmful and toxic to human beings and the environment. Therefore, they must be removed from wastewater and drinking water. Many techniques have been employed to remove heavy metal ions, including adsorption, chemical precipitation, electro-dialysis, ion exchange and membrane separation. Table 1 summarizes the general separation processes and their application for heavy metal removal [3].

Adsorption is a well known technique widely employed for separation and purification. In removing heavy metal ions from aqueous solutions, adsorbents can bind and capture heavy metal ions from the aqueous solutions. The key part of an adsorption process is the adsorbents. Thus, good adsorbents should be abundant and easy to process, and have high selectivity, large surface area and long service time [4].

Table 1. Separation techniques for removal of heavy metal ions from aqueous solution [Humphrey 1997]

Separation technique	Advantage	Disadvantage Regeneration needed		
Adsorption	Economical and efficient for dilute solution			
Chemical precipitation	Remove most heavy metal ions	Need to adjust pH and break down the complex		
Electrodialysis	Remove most ions with electric charge	Unsatisfactory for removal of chelated ions           metal         Fouling and regeneration		
Ion exchange	Easy removal of heavy metal			
Membrane separation	Excellent heavy metal removal	Membrane fouling cost		

# Experimental

Cross-linked copolymers of acrylic acid (partially neutralized) and acrylamide were synthesized by radical polymerization in aqueous solutions. These soft and wet hydrogel materials can easily swell in aqueous solutions due to the hydrophilic groups in the macromolecular chain. However, they are not soluble in water. These materials showed different sorption capacity for pure water and metal uptake. Copper sulfate was used as a model adsorbate in this research.

Pure water sorption

Figure 2 shows the results of pure water sorption as a function of macromolecular structure of cross-linked copolymers. In this three-dimensional chart, the two horizontal axes show the content (AAc %) in the co-monomers and the content (NMBAM %) of cross-linking agent used in the copolymer synthesis, respectively, and the longitudinal axis indicates the water sorption uptake (Swelling%).

$$S_{W=\frac{m_{w-m_0}}{m_0}}$$





It can be seen that the water sorption capacity (g/g-copolymer) of the hydrogel sample increases when the content of the acrylic acid in the comonomers increased about 8000 g/g is attained with polymer produced from only acrylic acid at 1.0 % cross-linking agent. Clearly, acrylic acid has a strong influence on the water sorption capacity of the copolymer hydrogels. The carboxyl groups in the acrylic acid exhibit a high capacity for holding water molecules compared to the amide of acrylamide. As expected, for any given AAc/AAm compositions, a decrease in the content of the cross-linking agent increases the water sorption capacity. The cross-linking affects directly the length of the polymer chain segment and the pore size of the cross-linked network.

### Sorption isotherm

Figures 3 show the sorption uptake of lead nitrate and water as a function of equilibrium concentration of the lead in the nitrate solution. At a relatively low concentration of lead ion in the solution, the equilibrium sorption uptake of lead nitrate increases drastically with an increase in the lead ion equilibrium concentration in the solution.



Figure 3. Sorption uptake of water in the copolymer as a function of equilibrium concentration of copper in the solution



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Figure 4 shows that the sorption data at low concentration range (<10 mg) can be represented by the Langmuir isotherm equation with a correlation coefficient (R2) of 0.972. It should be pointed out that the active sorptive sites, carboxyl groups, associate with lead ions to form chelating complexes with one or two. The functional carboxyl groups in the chain segments of the copolymer network cannot move freely toward lead ions to form complexes because the flexibility of chain segments of the copolymer declines once sorption occurs. Based on Langmuir isotherm, the maximum sorption capacity in the copolymer ( $q_{max}$ ) is 9.89 mg/g and the binding constant ( $K_L$ ) is 2.9 l/mg.

Figure 4 shows Raman spectra taken a different composition AAM/AAc (a:100/0, b:80/20 and c:60/40) the hydrogel. This figure depicts that the Raman intensity of most of the peaks decreases with the amount of with increasing of AAM. Figure 5 shows an enlargement of which was used for calculating composition of the hydrogel.





Fugure 4. Raman spectra of the hydrogel With a ratio of AAM/AAc a: 100/0, b: 80/20 and c: 60/40

Figure 5. Raman enlargement of which was used for calculating the composition of the hydrogel

The analysis of the composition of the hydrogel was performed using the amplified signals (Figure 5) of the spectrum  $(1226 \text{ cm}^{-1})$ , calculating the area under the curve of the signal.

## CONCLUSIONS

Copolymers of acrylic acid and acrylamide were synthesized by free radical polymerization in aqueous solutions. The copolymers were comprised of different contents of acrylic acid and were cross-linked with different amounts of NMBAM. These copolymers were tested for lead sorption for aqueous solutions. The following conclusions can be drawn from this research:

• The effect of macromolecular structure on water sorption and metal ion  $(Pb^{2+})$  uptake is systematically investigated.

• With an increase in the content of the acrylic acid, lead nitrate uptake increases, and water sorption decreases quickly and then gradually increases when the acrylic acid content is high enough. Lead ion uptake is accompanied with ions from the copolymer.

• With an increase in the content of the cross-linking agent, both copper sulfate uptake and water sorption decrease.

• At relatively low concentrations of Pb(NO3)2 in water, the copper sulfate sorption into the copolymer follows the Langmuir model.

• When lead ions to interact with carboxyl groups in the copolymer to form chelating complexes, the water sorption decreases substantially.

• The calculation of the compositions of the hydrogels by Raman spectroscopy is relatively simple, as long as they have non-overlapping signals in the spectrum.

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# BIOLOGICAL DEGRADATION BY TERMITES OF COMPOSITE MATERIALS PREPARED WITH PINE RESIDUES AND RECYCLED HDPE

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#### Abstract

Wood plastic composites (WPCs) manufactured by means of twin-screw extrusion were prepared to evaluate their resistance to biotic attack caused by termites native to the Yucatan Peninsula. Pine residues and recycled HDPE were used to prepare such composites. It has been reported that during exposure to accelerated weathering WPCs' surface is affected by the appearance of cracks, which constitute an ideal access route for such agents. Thus, composites exposed to 0, 1000 and 2000 hours of UVA-weathering were subjected to direct attack of biotic agents. FTIR, SEM, DSC and mechanical properties were used to study the effect of both degradation processes.

## Introduction

Although WPCs have been promoted as low-maintenance and high durability products [1], their use in construction industry is still subordinated to its performance, especially when exposed to outdoor environments [2]. It has been demonstrated that WPCs exposed to accelerated weathering may experience color change and cracks formation, affecting their aesthetic appeal as well as their mechanical properties [1]. Manufacturing methods also play an important role on determining WPCs properties. Parameters such as temperature, pressure, and flow rate may promote moisture absorption [3]. Additionally, it is widely known that unprotected wood can be attacked by a wide variety of biotic agents. In general, this action occurs as an extracellular process, catalyzed by enzymes [4]. There are three major types of enzymes involved in hydrolysis of cellulose (i.e., Endo-β-1,4-glucanases, β-Glucosidases and Cellobiohydrolases) [5]. Although insects never appear to be capable of forming cellobiohydrolases, some of them such as termites are said to digest a significant proportion of the cellulose (74-99%) and hemicellulose (65-87%) components of lignocellulose they ingest [6]. As termites search for food, they may penetrate and damage many noncellulose materials as well, including plastics, even if these do not serve as food source and cannot be digested. It is therefore not surprising that most plastics failed in tests for resistance to termites. Not only the mechanical hardness of plastics but also the surface structure of the material characterizes their durability against termite attack. Smooth and even rough surfaces are more likely to prevent termite attack, but the smallest cracks and crevices or ruffled surfaces and edges provide immediate access for termite mandibles. Therefore, investigating the effects of termite attack on weathered and unweathered composites is important for outdoor applications of WPCs. In this study three different materials, two of them manufactured by compression molding and one extruded, were exposed to the attack of higher termites native to the Yucatan Peninsula after 0, 1000 and 2000 hrs of accelerated weathering.

#### Experimental

Raw Materials: Pine residues (40 mesh flour from Maderas Bajce, Merida, Mexico), injection

grade recycled HDPE (MFI = 4.56 g/10 min) from Recuperadora de Plásticos Hernández (Merida, Mexico), Polybond 3009 (MAPE) as coupling agent, and Struktol TPW 113 as processing aid.

<u>WPC preparation</u>: HDPE, pinewood and additives were premixed and dried (105°C, for 24 hrs) before extrusion. Two different compositions based on 40 % by weight (wt.%) of wood, 60 wt.% of plastic, and 3 wt.% of Struktol (with respect to wood %) were prepared. One of them was added with 5 wt.% of Polybond with respect to wood %. Compounding was carried out in a conical twinscrew extruder (Brabender EPI-V5501). Composition without Polybond was extruded using a 4 cm long extrusion die of 2 mm in internal diameter fitted to the extruder, whereas the other was processed using a slot die (~ 10 mm long) and the die previously described. During extrusion, the screw speed was 50 rpm and the barrel and die temperatures were set at 140°C.

<u>Specimens for mechanical characterization</u>: Test samples were directly cut off from extrudates obtained using the slot die to be tested under flexion according to ASTM D 790 standard. Test samples of composites obtained using the cylindrical die were produced by compression molding. They were subjected to flexural, tensile, and Izod impact tests following ASTM Standards D 790, D 638 and D 256, respectively [7-9].

<u>Accelerated Weathering Tests</u>: Experiments were performed in an ATLAS UVCOM accelerated test device located at Centro de Investigaciones en Corrosión of the Autonomous University of Campeche (CICORR-UAC). The samples were exposed to UV/condensation cycles using 4 hours of UV light irradiation at 60°C with 340 nm fluorescent UV lamps, followed by 4 hours of condensation at 50°C. Mechanical properties evaluation, and FTIR, DSC and SEM analyses were carried out on 0, 1000 and 2000 hrs weathered samples.

<u>Biodegradation Test</u>: Weathered specimens were exposed to termites attack according to ASTM D 3345 standard test method [10]. Organisms directly attacked the samples during a maximum period of 30 days. Samples exposed during 15 and 30 days to biological attack were analyzed by FTIR, DSC, and SEM. Mechanical properties were also evaluated.

## **Results and Discussion**

The results of the mechanical characterization are presented in Tables 1 to 3. In general the results indicate that the drop in mechanical properties was higher during the first 1000 hours of exposure to accelerated weathering than during the second cycle of 1000 hours. The positive effect of the coupling agent is evident since, as it can be observed, there was a slightly increment on the mechanical properties raging from a 3 % (for flexural and tensile resistance) to 10 % (for impact resistance). Nevertheless, both compression-molded composites show similar drops in their mechanical properties. In regard to the manufacturing method, it has been previously reported that the surface layer of extruded composites contains less polymer than compression-molded ones. It would be expected that these materials (i.e., the extrudates) would absorb more water, thus, more cracks and crevices could appear, providing more access routes for termite mandibles than in compression-molded materials.

Exposure		Strength		Module			
time	(MPa)			(GPa)			
(hours)							
	Compression	Compression	Extruded	Compression	Compression	Extruded	
	molded (CA)	molded	(CA)	molded (CA)	molded	(CA)	
0	12.14	11.69	9.82	0.44	0.42	0.33	
1000	11.06	10.43	8.71	0.44	0.42	0.29	
2000	10.28	TBC	TBC	0.41	TBC	TBC	

Table 1. Flexural properties of 40 % wood-filled HDPE composites obtained by compression molding and extrusion
after 0, 1000 and 2000 hours of accelerated weathering.

CA: material with coupling agent.TBC (to be completed).

Table 2. Tensile properties of 40 % wood-filled HDPE composites	obtained by compression molding after 0, 1000
and 2000 hours of accelerated	weathering.

Exposure time	Stre	ngth	Module		
(hours)	(M	Pa)	(GPa)		
	Compression Compression		Compression	Compression	
	molded (CA)	molded	molded (CA)	molded	
0	15.30	14.79	0.37	0.37	
1000	13.56	13.06	0.36	0.37	
2000	13.37	12.44	0.37	0.36	

CA: material with coupling agent

 Table 3. Izod impact properties of 40 % wood-filled HDPE composites obtained by compression molding after 0, 1000 and 2000 hours of accelerated weathering.

Exposure time	Strength				
(hours)	(J/m)				
	Compression molded (CA)	Compression molded			
0	13.55	12.15			
1000	12.97	11.26			
2000	TBC	TBC			

CA: material with coupling agent .TBC (to be completed).

The results of the DSC analysis are presented in Figure 1. This technique was used to measure the effects of aging on transition temperatures and polymer matrix microstructure. Figure 1 shows thermograms for weathered and unweathered composites. New thermal energy absorption peaks (shoulders) and a broadening of the endotherm graph were observed for weathered materials due to degradation. These results can be attributed to changes in crystallites sizes and molecular weight differences caused by chain breaking and secondary recrystallization. This kind of shoulders has been reported before for HDPE [11].

SEM micrographs are presented in Figure 2, corresponding to aged and non-aged composites. The surface of non-exposed composites was initially smooth (Fig. 2a and b). However, after 1000 hrs of accelerated weathering (Fig. 2c and d) surface cracks were apparent. It is possible to appreciate unprotected fibers that could constitute an entrance route for termites in the material.



rigure 1. Disc merinograms of unweathered and weathered compression-molded composites.



Figure 2. SEM micrographs of compression-molded composites: (a) Unweathered without coupling agent, (b) unweathered with coupling agent, (c) 1000 hrs exposed without coupling agent, and d) 1000 hrs exposed with coupling agent.

#### Conclusions

Partial results indicate that after accelerated weathering cycles composites are degraded. SEM micrographs show that after aging the initially smooth surface of composites was degraded, and cracks and crevices appeared on it. DSC thermograms confirm that composites were degraded, evinced by broadened endotherms and appearance of new peaks (shoulders) that could be related to chain scission, molecular weight changes and secondary recrystallization. Finally, the decrease of mechanical properties also demonstrates that a degradation process occurred. Partial results suggest that a biotic attack caused by termites is possible because cracks and crevices could provide access to their mandibles, giving place to a biological degradation process.

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# EFFECT OF PHANEROCHEATE CHRYSOSPORIUM ATTACK ON MECHANICAL PROPERTIES OF A COMPOSITE PREPARED WITH COIR FIBERS AND RECYCLED HDPE

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#### Abstract

Solid urban wastes are one of the main sources of contamination globally and locally. An alternative to solve this problem is using them to obtain added-value products. It is known that discarded fibers from the husk of coconut (i.e., coir) generally have good mechanical properties, which can be useful to fabricate different products. However, these products can be affected mechanically and superficially by microorganisms such as white-rot fungus. The present work deals with the preparation of composites by extrusion with 60 % of recycled HDPE and 40 % of coir. It was evaluated the effect of *Phanerocheate chrysosporium* (Pc) on the materials' mechanical properties, before and after subjecting them to weathering by using an accelerated test device. The materials were characterized by FTIR and SEM. Tensile and flexural mechanical performance was evaluated following ASTM standard tests. It was observed signs of damage by Pc on the surface of the obtained materials. On the other hand, the decay on the mechanical performance of materials not subjected to weathering was not significative due to inoculation with Pc.

#### Introduction

An alternative to solve the problems related with excessive accumulation of solid urban wastes is using these materials to transform them into useful products for industry and society. Among many possibilities for recycling is to produce natural fibers-plastic-based composite materials, with potential applications in the construction and furniture markets, economy sectors that have grown rapidly for over 25 % since 1998 [1]. Specific applications for these kinds of materials may be found in gardening, indoor and outdoor furniture, and ornamentation, among many others [1]. Natural fibers are susceptible to biological degradation by fungi. In this way, some natural fibers-based composites can be affected when the fungi subsistence conditions are met, namely moisture, temperature, etc. [2]. For this reason, the properties of plastic-based products fabricated with, let us say, coir fibers can be affected when they are intended for outdoor use, precisely because the weather will promote the conditions needed such that these materials suffer microbiological deterioration, affecting their expected performance, for instance esthetic-related issues and mechanical resistance. Specifically, the white-rot fungus, *Phanerocheate chrysosporium* (Pc), affects coir properties [3, 4], which means that it will probably affect the performance of a polymer composite prepared with this type of fiber.

#### Experimental

#### Materials

- Reinforcement/filler: Coir fibers from coconut palm tree ecotype MXPT2 (Mexican Pacific Tall 2) provided by Coirtech (Tecomán, Colima, México).

- Polymer matrix: Recycled high density polyethylene (HDPE-R), with MFI = 4.56 g x  $10^{-1}$  min<sup>-1</sup>

supplied by Recuperadora de Plásticos Hernández (Mérida, Yucatán, México).

- Coupling polymer (AA): Maleic anhydride grafted HDPE (Polybond 3009), supplied by Brenntag México, S.A. de C.V. (MFI = 5 g x  $10^{-1}$  min<sup>-1</sup>, density = 950 kg m<sup>-3</sup>, Tm = 127°C, maleic anhydride level = 1 % by weight).

- Processing aid (AP): Struktol TPW113 from Struktol Company of America.

- Biological treatment: It was used a white-rot fungi strain, *Phanerocheate chrysosporium* (Pc), cultivated at the Biotechnology Unit of Centro de Investigación Científica de Yucatán (UBT-CICY). The reactive substances used to inoculate the composites with Pc are described in the ASTM G21-96 (2002) standard test method.

## **Composites preparation**

The coir fibers were milled and then screened in a TYLER nest of sieves using a W.S. TYLER RO-TAP sieve shaker to obtain approximate particle sizes ranging from 0.297 to 0.420 mm. HDPE-R, AA, and AP were milled with BRABENDER equipment fitted with a screen with holes of 1 mm in diameter. Afterwards, a blend was prepared as follow: 60 % by weight (wt.%) of HDPE-R, 40 wt.% of coir, and 5 and 3 wt.% of AA and AP with respect to the coir content, respectively. The blend was then processed using a BRABENDER laboratory conical twin-screw extruder with three heating zones. Rods of approximately 3 mm in diameter were obtained by using a 4 cm long extrusion die of 2 mm in internal diameter fitted to the extruder. The processing temperature was 140°C. The resultant extrudates were pelletized using a BRABENDER laboratory pelletizer machine.

## **Test samples preparation**

Tensile and flexural test specimens were prepared by compression molding. The tensile specimens were obtained by using a mold with specific dimensions to obtain type V specimens, according to the ASTM D638 standard test method. Flexural specimens were obtained by machining flat plaques to produce the samples with the dimensions specified in the ASTM D790 method. Two sets of specimens were prepared as indicated in Table 1.

Type of specimens	Type of test	Control (T0)	T1
Group I: Directly inoculated with	Tensile	10	10
Pc. No exposure to accelerated weathering	Flexural	10	10
Group II: Previous exposure to	Tensile	10	10
accelerated weathering and then inoculated with Pc	Flexural	10	10

 Table 1. Number of specimens prepared for each group

## Accelerated weathering tests

Group II specimens were exposed in an ATLAS/UVCON accelerated test device located at Centro de Investigaciones en Corrosión of the Autonomous University of Campeche (CICORR-UAC). The exposure time was 1000 hrs, using 4 hrs condensation and UV irradiation cycles, respectively. UVA-340 lamps were used for the experiments, following the procedure specified in ASTM

#### G154-00 and ASTM D4329-99 standard methods.

#### **Composites inoculation and incubation**

General sterilization was carried out at 120°C for 15 min. Inoculation with Pc was performed on the specimens' surface according to the ASTM G21-96 (2002) test method. The amount of spores inoculated on the samples was determined taking into account the area of each type of specimen to be exposed. The incubation period was 28 days, whereas the incubation room temperature was 30–32°C. Afterwards, the specimens for analysis were safely stored, and general disinfection was carried out using a 10 % v/v chorine solution and ethanol.

## Chemical and morphological analyses, and mechanical properties characterization

FTIR was used for the chemical analysis of the specimens' surfaces inoculated with Pc. A FTIR Nicolet Protege 460 instrument was used, together with a cell to obtain the composites spectra. Non-inoculated surfaces with Pc were also analyzed to serve as control specimens. SEM was used for the morphological analysis. A JEOL 6360 LV instrument operated at 20 kV was used. The composites tensile and flexural mechanical properties were evaluated using an INSTRON universal testing machine (Model 1125), following the procedure indicated in ASTM D-638 and ASTM D790 standard test methods, respectively. All the experiments were performed at room temperature, previously conditioning the specimens (i.e., relative humidity = 45 %, temperature =  $23^{\circ}$ C, for 24 hrs).

## **Results and Discussion**

Figures 1 and 2 show IR spectra of the composite unexposed and exposed to accelerated weathering, respectively. Both Figures show an increase of the intensity of the peak at 1645 cm<sup>-1</sup> that can be associated to the presence of peroxidase enzymes released by Pc, and to changes in the lignin chemical structure [5]. Magnification in the interval 3333-3358 cm<sup>-1</sup> can also be observed, which indicates the presence of hydroxyl groups [5, 6]. Lignin biodegradation is based on the production of oxidative species such as the formation of hydroxyl radicals during the growing of Pc on the composite, which initiates biodegradation of it [6]. In the same way, it is noticeable a higher amplitude and intensity of the peaks in the interval 1625–1820 cm<sup>-1</sup>, which corresponds to the presence of carbonyl groups [5-7]. It has been reported that this can indicate biological attack on the composites by white-rot fungi [5], although for the material exposed to accelerated weathering (Fig. 2), it can also be related to photodegradation [8, 9]. The results of the SEM analysis are presented in Figure 3. From Fig. 3a, defects can be observed on the surface of a control specimen unexposed to accelerated weathering. It is believed that in these flaws the materials are more susceptible to Pc attack as shown in Fig. 3b. On the other hand, Fig. 3c shows severe damages on the material surface due to exposure to accelerated weathering. The cracks observed will facilitate access of Pc to reach the coir fibers to consume them as carbon source [2, 10].





**Figure 2.** FTIR spectrum of a material exposed to accelerated weathering. T0CI: Control (specimen not inoculated with Pc). T1CI: Inoculated specimen with Pc, followed by incubation for 28 days.

The results of the mechanical characterization are presented in Table 2. It was observed a higher decrease of flexural properties than that observed for the tensile properties. However, the overall decay of the mechanical performance was lower than 25 %, so it cannot be considered significative, especially if compare these results with other works that have reported reductions of the elastic modulus higher than 50 %. As in the present work, the decay of the mechanical performance was also associated with moisture absorption [2, 11].

Table 2. Mechanical characterization results for specimens exposed (CI) and unexposed (SI) to accelerat	ed
weathering. SD: Standard deviation	

	Tensile				Flexural			
	Resistance (MPa)	SD	Modulus (GPa)	SD	Resistance (MPa)	SD	Modulus (GPa)	SD
TOSI	14.84	1.4587	3.30	0.3177	15.31	0.5939	5.88	0.2193
T1SI	13.31	1.0262	2.72	0.1671	14.06	0.3843	4.48	0.0623
TOCI	13.40	2.2819	2.66	0.2745	14.84	1.4291	5.22	0.2364
T1CI	13.27	0.8613	2.52	0.5249	12.86	0.1557	4.01	0.0583



**Figure 3.** SEM micrographs. (a) Control specimen, unexposed to accelerated weathering (T0SI). (b) Specimen unexposed to accelerated weathering inoculated with Pc (T1SI). (c) Control specimen, exposed to accelerated weathering (T0CI). (d) Specimen exposed to accelerated weathering inoculated with Pc (T1CI).

#### Conclusions

The results indicate that the surface of the coir fibers-recycled HDPE composite was mostly affected by Pc, especially when it was exposed to accelerated weathering. The diminishment of mechanical properties was not significative, which means that the resultant composite perhaps will not be affected by other types of fungi. However, more experimentation is needed in order to prove it.

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# EFFECT OF MOISTURE ABSORPTION AND DESORPTION ON THE MECHANICAL PROPERTIES OF A COMPOSITE BASED ON PINE RESIDUES AND HDPE

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#### Abstract

Wood-polymer composites (WPCs) can be used as alternative materials in construction industry. However, the effect of weather is an important aspect that should be studied to understand how they are affected during their use for a specific application. This work deals with evaluating the effect of moisture absorption and desorption cycles occurring in a WPC, obtained by extrusion, on its mechanical properties as a function of coupling agent %, applied UV irradiation, and number of moisture cycles. Composites with pine residues and virgin HDPE were prepared. They had 5, 2.5 and 0 % of a coupling agent, respectively. Tensile and flexural specimens of these materials were exposed to UV irradiation in a weathering accelerated test device, and to absorption and desorption of moisture. The specimens were also analyzed by SEM. The presence of cracks on the materials' surface was observed due to UV irradiation. Also, it was noticed that the combined effect of irradiation and moisture cycles was higher than that due only to absorption and desorption of moisture. Significative decay on the mechanical properties was not observed.

#### Introduction

Lignocellulosic-rich fillers provide added benefits to polymer-based products with regard to lightness, mechanical resistance, and rigidity [1]. Many of these products are intended for outdoor applications; hence they are exposed to weather conditions such as UV light, moisture, and temperature that can affect their performance [2]. When these products are fabricated with wood residues, one of their main problems is wood susceptibility to absorb moisture, which can degrade them, thereby limiting their potentials. For instance, changes of humidity levels will promote wood residues to experience moisture absorption-desorption cycles, causing swelling and then shrinking repeatedly, affecting in this way the products mechanical performance [3, 4]. These moisture cycles, simultaneously occurring together with residual stresses generated within a polymer composite has been defined as a mechano-sorption phenomenon; and is responsible for damaging the wood-matrix interphase, leading to resistance and rigidity losses [3, 4]. The main aim of this study is to evaluate the effect of moisture absorption-desorption cycles on the mechanical properties of a pine residues-HDPE-based composite as a function of coupling agent content, applied UV irradiation, and number of moisture cycles.

#### Experimental

<u>Raw materials</u>: Pine residues (sawdust) provided by BAJCE (Merida, Mexico), HDPE grade 56035 from Petroquímica Morelos, maleic anhydride grafted HDPE (Polybond 3009) as coupling polymer supplied by Brenntag México, S.A. de C.V., and Struktol TPW113 from Struktol Company of America as processing aid.

<u>Composites preparation</u>: Wood residues were milled with a Pagani granulating machine (Model 1520) fitted with a screen plate drilled with holes of 1 mm in diameter. Afterwards, they were

screened in a TYLER nest of sieves (meshes # 20, 30, 40, and 50), using a W.S. TYLER RO-TAP sieve shaker (Model RX-29). Wood residues retained on mesh # 40 (mesh opening = 0.430 mm) was used. HDPE, Polybond, and Struktol were milled with BRABENDER equipment (Model 880804) fitted with a screen with holes of 1 mm in diameter. Three composites were prepared with 40 % by weight (wt.%) of wood, and 60 wt.% of HDPE, and 3 wt.% of Struktol (with respect to wood %). One composite did not have Polybond, whereas the second and the third ones had 2.5 and 5 wt.% with respect to wood %, respectively. The composites were obtained using a BRABENDER laboratory conical twin-screw extruder with three heating zones. Rods of approximately 3 mm in diameter were obtained by using a 4 cm long extrusion die of 2 mm in internal diameter fitted to the extruder. The processing temperature was 180°C, and the screws' speed was set at 50 rpm. The resultant extrudates were pelletized using a brizontal mixer with a helical agitator (Intertécnica Co., Model ML-5) and a capacity of 5 liters. The blends were prepared mixing the raw materials for 5 min.

<u>Test samples preparation</u>: Test specimens were prepared from the composites' pellets previously compounded. Tensile and flexural specimens were prepared by compression molding. The tensile samples were obtained by using a mold with specific dimensions to obtain type V specimens, according to ASTM-D638 standard test method. Flexural specimens were obtained by machining flat plaques to produce samples with the dimensions specified in ASTM-D790 method. CARVER manual (tensile samples), and automatic (flexural samples) hydraulic presses were respectively used. The molding was performed at 160°C and at a compression force of about 44,482 N (10,000 lbf) for the tensile samples and 26,689 N (6000 lbf) for the flexural ones.

<u>Accelerated weathering tests</u>: Specimens were exposed in an ATLAS/UVCON accelerated test device located at Centro de Investigaciones en Corrosión of the Autonomous University of Campeche (CICORR-UAC). The exposure temperature was 60°C during one and two weeks, respectively, applying 24 hrs of continuous UV irradiation. UVB-313 lamps were used for the experiments. All the samples for the experiments were previously weighed. Test standards ASTM-D618, G147-02, G151, and G154 were followed.

<u>Moisture absorption-desorption experiments</u>: Specimens exposed and unexposed to accelerated weathering were subjected to 4 and 8 moisture absorption-desorption cycles according to ASTM-D570 and D5229 standard test methods. Each cycle involves immersing the samples in distilled water for 10 days, and further drying for 5 days, both at  $60^{\circ}$ C. Variation of the specimens' weight was monitored during the experiments.

<u>Mechanical properties characterization and morphological analysis</u>: Tensile and flexural tests were performed on specimens subjected to UV irradiation during 2 weeks, and to 4 and 8 moisture cycles. The experiments were carried out using an INSTRON universal testing machine (Model 1125), following the procedure indicated in ASTM D-638 and ASTM D790 test methods, respectively. Afterwards, the gold-coated specimens were analyzed by SEM, using a JEOL 6360LV microscope.

## **Results and Discussion**

The results of the mechanical characterization are presented in Table 1.

Tensile Specimens	<b>Resistance (MPa)</b>	Modulus (GPa)
Without Polybond	22.89 (±0.68)	4.13 (±0.44)
Without Polybond (2 weeks UV irradiation)	16.71 (±0.65)	3.76 (±0.54)
Without Polybond (8 moisture cycles)	18.89 (±0.99)	2.25 (±0.25)
Without Polybond (2 weeks UV irradiation) / 8 moisture cycles	16.88 (±0.62)	2.05 (±0.21)
2.5 wt.% of Polybond	21.47 (±0.91)	4.92 (±0.56)
2.5 wt.% of Polybond (1 week UV irradiation) /4 moisture cycles	17.65 (±0.91)	2.52 (±0.35)
5 wt.% of Polybond	24.23 (±0.65)	4.59 (±0.42)
5 wt.% of Polybond (2 weeks UV irradiation)	17.28 (±1.98)	4.49(±0.44)
5 wt.% of Polybond (8 moisture cycles)	20.42 (±0.73)	2.45(±0.37)
5 wt.% of Polybond (2 weeks UV irradiation) / 8 moisture cycles	17.82 (±0.87)	2.46(±0.20)
Flexural	Resistance (MPa)	Modulus (GPa)
Flexural Without Polybond	<b>Resistance (MPa)</b> 15.7 (±0.39)	<b>Modulus (GPa)</b> 6.48 (±0.2)
Flexural         Without Polybond         Without Polybond (2 weeks UV irradiation)	Resistance (MPa)           15.7 (±0.39)           12.45 (±0.58)	Modulus (GPa) 6.48 (±0.2) 5.52 (±0.58)
Flexural         Without Polybond         Without Polybond (2 weeks UV irradiation)         Without Polybond (8 moisture cycles)	Resistance (MPa)           15.7 (±0.39)           12.45 (±0.58)           12.69 (±0.78)	Modulus (GPa) 6.48 (±0.2) 5.52 (±0.58) 3.69 (±0.18)
Flexural         Without Polybond         Without Polybond (2 weeks UV irradiation)         Without Polybond (8 moisture cycles)         Without Polybond (2 weeks UV irradiation) / 8 moisture cycles	Resistance (MPa)           15.7 (±0.39)           12.45 (±0.58)           12.69 (±0.78)           10.26 (±0.24)	Modulus (GPa) 6.48 (±0.2) 5.52 (±0.58) 3.69 (±0.18) 3.09 (±0.12)
FlexuralWithout PolybondWithout Polybond (2 weeks UV irradiation)Without Polybond (8 moisture cycles)Without Polybond (2 weeks UV irradiation) / 8 moisture cycles2.5 wt.% of Polybond	Resistance (MPa)           15.7 (±0.39)           12.45 (±0.58)           12.69 (±0.78)           10.26 (±0.24)           15.12 (±0.83)	Modulus (GPa) 6.48 (±0.2) 5.52 (±0.58) 3.69 (±0.18) 3.09 (±0.12) 5.99 (±0.33)
FlexuralWithout PolybondWithout Polybond (2 weeks UV irradiation)Without Polybond (8 moisture cycles)Without Polybond (2 weeks UV irradiation) / 8 moisture cycles2.5 wt.% of Polybond2.5 wt.% of Polybond (1 week UV irradiation) /4 moisture cycles	Resistance (MPa)           15.7 (±0.39)           12.45 (±0.58)           12.69 (±0.78)           10.26 (±0.24)           15.12 (±0.83)           11.06 (±0.65)	Modulus (GPa) $6.48 (\pm 0.2)$ $5.52 (\pm 0.58)$ $3.69 (\pm 0.18)$ $3.09 (\pm 0.12)$ $5.99 (\pm 0.33)$ $3.20 (\pm 0.21)$
FlexuralWithout PolybondWithout Polybond (2 weeks UV irradiation)Without Polybond (8 moisture cycles)Without Polybond (2 weeks UV irradiation) / 8 moisture cycles2.5 wt.% of Polybond2.5 wt.% of Polybond (1 week UV irradiation) /4 moisture cycles5 wt.% of Polybond	Resistance (MPa) $15.7 (\pm 0.39)$ $12.45 (\pm 0.58)$ $12.69 (\pm 0.78)$ $10.26 (\pm 0.24)$ $15.12 (\pm 0.83)$ $11.06 (\pm 0.65)$ $16.43 (\pm 0.46)$	Modulus (GPa) $6.48 (\pm 0.2)$ $5.52 (\pm 0.58)$ $3.69 (\pm 0.18)$ $3.09 (\pm 0.12)$ $5.99 (\pm 0.33)$ $3.20 (\pm 0.21)$ $6.38 (\pm 0.22)$
FlexuralWithout PolybondWithout Polybond (2 weeks UV irradiation)Without Polybond (8 moisture cycles)Without Polybond (2 weeks UV irradiation) / 8 moisture cycles2.5 wt.% of Polybond2.5 wt.% of Polybond (1 week UV irradiation) /4 moisture cycles5 wt.% of Polybond5 wt.% of Polybond (2 weeks UV irradiation)	Resistance (MPa) $15.7 (\pm 0.39)$ $12.45 (\pm 0.58)$ $12.69 (\pm 0.78)$ $10.26 (\pm 0.24)$ $15.12 (\pm 0.83)$ $11.06 (\pm 0.65)$ $16.43 (\pm 0.46)$ $13.56 (\pm 0.49)$	Modulus (GPa) $6.48 (\pm 0.2)$ $5.52 (\pm 0.58)$ $3.69 (\pm 0.18)$ $3.09 (\pm 0.12)$ $5.99 (\pm 0.33)$ $3.20 (\pm 0.21)$ $6.38 (\pm 0.22)$ $5.66 (\pm 0.22)$
FlexuralWithout PolybondWithout Polybond (2 weeks UV irradiation)Without Polybond (8 moisture cycles)Without Polybond (2 weeks UV irradiation) / 8 moisture cycles2.5 wt.% of Polybond2.5 wt.% of Polybond (1 week UV irradiation) /4 moisture cycles5 wt.% of Polybond5 wt.% of Polybond (2 weeks UV irradiation)5 wt.% of Polybond (2 weeks UV irradiation)	Resistance (MPa) $15.7 (\pm 0.39)$ $12.45 (\pm 0.58)$ $12.69 (\pm 0.78)$ $10.26 (\pm 0.24)$ $15.12 (\pm 0.83)$ $11.06 (\pm 0.65)$ $16.43 (\pm 0.46)$ $13.56 (\pm 0.49)$ $13.71 (\pm 0.72)$	Modulus (GPa) $6.48 (\pm 0.2)$ $5.52 (\pm 0.58)$ $3.69 (\pm 0.18)$ $3.09 (\pm 0.12)$ $5.99 (\pm 0.33)$ $3.20 (\pm 0.21)$ $6.38 (\pm 0.22)$ $5.66 (\pm 0.22)$ $4.19 (\pm 0.24)$

Table 1. Results of the mechanical characterization

In general it can be noticed diminishment of the resistance and modulus for composites without and with 5 wt.% of Polybond (2 weeks UV irradiation). The tensile and flexural resistance, as well as the modulus for the composite with 2.5 wt.% of Polybond (irradiated and subjected to 4 moisture cycles) decreased about 18 and 46 %, respectively. The modulus for the composites without and with 5 wt.% of Polybond (subjected to 8 moisture cycles) was similar to that for composites exposed to 2 weeks of UV irradiation, and subjected to 8 moisture cycles. However, when it was irradiated and subjected to moisture, their resistance was lower than that obtained when the composite was only subjected to moisture cycles. This is attributed to moisture absorption as it was observed in other reports [5-8]. Perhaps this happens because the water plasticizes the wood particles, which in theory provide rigidity to the composite. As it has been reported [6], the increase of the resistance and modulus (tensile and flexural) when a coupling agent is used, is because it improves adhesion between the filler and the polymer matrix (providing stronger interphases), increasing in this way the composites mechanical properties. The decay of the tensile and flexural properties for the composites exposed to UV irradiation could be due to cracks generated on the specimens' surfaces as consequence of degradation reactions (e.g., polymer oxidation, chains ruptures, and crosslinking) occurring within the composite. It can be noticed however, that the decay of the mechanical properties after exposure to irradiation is not significative as we believe that the damage occurs mainly on the composites' surfaces. On the other hand, the negative effect of the moisture cycles on the mechanical properties is due to the

mechano-sorption phenomenon, which weakens the wood-polymer interphase.



The results of the morphological analysis are presented in Figure 1.

**Figure 1**. SEM micrographs of specimens subjected to different treatments: Composite without Polybond: a) Not irradiated surface, b) Irradiated surface, and c) Fracture surface. Composite with 5 wt.% of Polybond: e) Not irradiated surface, f) Irradiated surface, and g) Fracture surface. Composite with 2.5 wt.% of Polybond: d) and h) Irradiated surface and subjected to moisture cycles.

From Fig. 1 it can be observed the presence of cracks as a result of polymer degradation (Figs. 1b and f). Similar results have been obtained by other researchers [9]. "Unprotected" wood particles can also be observed as well as unshelling-like signs on the composite surface (i.e., the polymer matrix), which is not observed in Figs. 1a and e. It is also noticeable that the composite surface is damaged to a greater extent when Polybond was not used (Fig. 1b), contrasting with the composite that had it (Fig. 1f). Figure 1 also shows fibril-like features or "scabs" on the wood for composites containing Polybond (Fig. 1g). When the coupling agent was not used only the wood surface is observed (Fig. 1c). In general, these results indicate that the composites exposed to UV irradiation and subjected to moisture cycles were more damaged than those that were only irradiated (Figs. 1d and h).

## Conclusions

The mechanical properties of pine residues-HDPE-based composites were negatively affected to a greater extent due to combined exposure to UV irradiation and moisture cycles in comparison to the effect caused by subjecting the composites to these treatments separately. The decrease of modulus and resistance was attributed to moisture absorption, and combined exposure to UV irradiation and moisture cycles, respectively.

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# SYNTHESIS AND CHARACTERIZATION OF HIGH IMPACT POLYSTYRENE FROM HETEROGENEOUS STYRENE-RUBBER-POLYSTYRENE SOLUTION:INFLUENCE OF PS CONCENTRATION ON THE PHASE INVERSION, MORPHOLOGY AND IMPACT STRENGTH

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#### Abstract

High Impact Polystyrene (HIPS) was synthesized by free radical polymerization through the bulk suspension technique. Polybutadiene (PB) and/or polybutadiene-b-styrene copolymer (PB-b-PS) (8%) with a composition of PB:PS = 70:30 were used as impact modifiers in the presence of 7.5 wt-% of polystyrene (PS) and styrene monomer. Reference HIPS without PS was also synthesized. The interval of phase inversion (PI) was determined through the evolution of the morphology by transmission electron microscopy (TEM), the conversion (X), gel content (GC) and grafting degree (GD) were gravimetrically determined and impact strength (IS) tests were performed. When PS was added from the beginning of the reaction the PI shifted to earlier values of conversion (X= 0.19) in comparison with the reference HIPS (X=0.32). The morphology of the reference HIPS was of the core shell type and in the case of adding PS and SB copolymer at the beginning of the reaction, the morphology at the PI interval changes to the salami type, attributed to an increase in the interfacial tension between the phases. Moreover, in the presence of additional stirring, it changes from salami to core-shell type due to a poor stability as a consequence of a poor grafting degree. Meanwhile, the final size and volume fraction of the disperse phase increases 39 and 13 %, respectively, with respect to the reference HIPS and IS increased from 37 (reference HIPS) to 45 J/m. Similar behavior was present for HIPS synthesized using PB.

#### Introduction

High impact polystyrene (HIPS) is a heterophasic polymer constituted by a continuous polystyrene phase and a disperse rubber, generally polybutadiene (PB), phase. Historically [1-4], HIPS was synthesized from a PB/Styrene homogenous solution by means of radical polymerization by bulk or bulk-suspension methods. During the HIPS polymerization several phenomena are present, at beginning, the system is homogenous, but at low conversion ( $\sim 2\%$ ) the separation of phases occurs and a continuous styrene-rubber phase (SRP) coexists with a disperse styrene-polystyrene phase (SPP) by means of the graft copolymer (PB-g-PS) produced in situ. When the volume of both phases becomes equal a co-continuous phase is present. As polymerization proceeds, the volume of the SPP increases and the volume of the SRP decreases and the phase inversion phenomenon occurs. At this moment and immediately after PI, the SPP becomes the continuous phase and the SRP the disperse phase. At this point the morphology of HIPS is established and its type is preserved. Generally, the morphology can be of the salami type (with PS multi-occlusions) or core shell type (PS mono-occlusion) depending on the precursor rubber used. After phase inversion the size of rubber particles can be reduced by two main factors: coagulation of the occlusions into the rubber particle or by migration of PS occluded to the PS matrix [4]. The control and development of HIPS morphology have been extensively studied, where the effect of parameters like stirring rate, PB content, radical initiator concentration, the use of transfer agents, PB molecular weight, and temperature, among others, were reported. However, all of these studies were focused on the typical HIPS synthesis from a PB/Styrene homogeneous solution. This research deals with the synthesis of HIPS from a PB/PS/Styrene heterogeneous solution and the effect of PS content on the morphology development and impact strength.

## Experimental

## **HIPS** synthesis

HIPS were synthesized using a graded styrene-butadiene block copolymer (SB) or polybutadiene (PB) by the bulk-suspension technique in a one gallon capacity stainless steel reactor, with an anchor-turbine stirrer and at room temperature: i) a fixed 8 wt-% of rubber and 7.5 wt-% of polystyrene were dissolved into styrene at a stirring rate of 20 rpm until the total dissolution; ii) 0.1 wt-% of BPO and 0.1 wt-% of Lupersol 233 M75 were added to the reaction mixture, the stirring rate and temperature were increased to 40 rpm and 90°C, respectively, and the stage of bulk pre-polymerization took place until the monomer conversion (X) was approximately 0.35-0.40; iii) During the last stage some samples were extracted at 25 min to determine X, and the polymerization was carried out up to total monomer conversion for each sample in bulk. In the case of styrene-butadiene block copolymer (SB) as the rubber 2 reactions in presence of PS were performed (HIPS(SB/PS)R1 and HIPS(SB/PS)R2). With PB only one reaction is shown (HIPS(PB/PS)). Reference HIPS without PS was also synthesized (HIPS/PB and HIPS/SB).

#### Characterization

Monomer Conversion was determined by dissolving 2-5g of sample in 25 mL of toluene, followed by precipitation in 300 mL of methanol. In order to obtain solely styrene conversion, the 8 wt-% of rubber and the 7.5 wt-% of PS added into the reaction were subtracted from the initial weight value of the sample considered. Thus, conversion is indicated as the ratio of the amount (g) of the precipitated sample, to the amount (g) of the initial sample.

Morphology of the samples was examined by transmission electron microscopy (TEM) using a JEOL or TITAN microscope. The examined samples were first cut under cryogenic conditions with a Leica Ultracut ultramicrotome with a diamond knife to a thickness of ca. 70 nm and stained with osmium tetraoxide. The average particle diameter (Dp) and the volume fraction of the disperse phase ( $\Phi$ ) were determined using the Image Analyzer Software "Image Pro 3.0". Impact strength was determined according to ASTM D-256.

#### **Results and Discussions**

Figure 1 shows the evolution of conversion as a function of polymerization time and the free radical concentration [R], calculated from equation 1, for the different synthesized HIPS. It can be observed that the conversion remains without significant variation for the HIPS synthesized in the presence of 7.5 wt-% of PS, however it is higher in the case of the reference HIPS.

This behavior can be attributed to the higher viscosity of the reaction medium in the presence of PS that limits the access of monomer molecules onto the growing chains due to a poor diffusion in a high viscous medium.

$$\left[R^*\right] = \frac{1}{k_p(1-x)} \frac{dx}{dt}$$
Eq. (1)

In the case of free radical concentration, it shows a similar behavior to that observed for the conversion, however, in this case the lowest concentration of radicals in the polymerization system in the presence of PS is mainly because in this case a lower concentration of initiator was used, since the recipes were adjusted to 1% by weight but only with respect to rubber and styrene monomer, hence in both reactions with PS, it is observed exactly the same concentration of radicals.



Figure 1. a) Conversion as a function of time and, b) Free Radical Concentration [R] as a function of conversion, for the synthesized HIPS.

On the other hand, Fig. 2 shows the morphological evolution for different synthesized HIPS. It can be observed that in the range of conversion evaluated (X = 0.19 to 0.32), during the reference HIPS polymerization, different phenomena are observed i) phase separation, ii) co-continuous phases and iii) phase inversion, and the formation of a characteristic morphology which is expected for the synthesis of HIPS with the type of copolymer used. In this sense, this morphology generally results in a phase transformation from the laminar co-continuous morphology to a core-shell type [2].

However, for HIPS synthesized in the presence of PS the behavior was totally different. It can be observed (see Fig. 2) a shift of the phase inversion at lower conversions (X = 0.18 to 0.19) accompanied by a completely different morphology than the one expected (core-shell, mono-occluded). In this case the morphology has multiple occlusions, similar to the salami type morphology. However, when the agitation continues this morphology is not preserved with the polymerization time mainly due to two factors, first to the instability of the particle by the low degree of grafting reached (88%) at the point of phase inversion with respect to that achieved during the polymerization of reference HIPS (160%), causing the particles to break and collapse into a smaller size and second, because this lower grafting degree fails to provide sufficient barrier between the phases which promotes the dissemination of species between the phases [4], mainly polystyrene species move from the phase styrene/ rubber to the phase styrene/PS thus reducing the particle size from 1 micron to the order of 200 nm.

Whether the change from the mass to the suspension stage was performed at the same time, the end result is an increase in both particle size and in impact resistance of materials, achieving an increase in particle size from 130 nm (HIPS/SB) to 188 nm (HIPS (SB/PS)R1 and R2) which represents a 40% increase.



**Figure 2.** Morphological development by TEM for a) HIPS/SB at X=0.19, X=0.28 and X=0.32, b) HIPS(SB/PS)R1 at X=0.19, X=0.27 and X=0.32 and c) HIPS(SB/PS)R2 at X=0.18, X=0.27 and X=0.32 (bar scale at 1micron).

In the case of the impact strength, it increased from 37 J/m (HIPS/SB) to 45 and 46 J/m (HIPS(SB/PS)R1 and R2, respectively), representing a 14% of increase in this property. Although the salami-type morphology was not preserved during the synthesis of HIPS in the presence of PS, this analysis allow the study of the system but now withdrawing the agitation and continue in a static bulk polymerization or suspension, in order to obtain particles in the order of microns, if the morphology observed in the range of phase inversion would preserve.



Figure 3. Final morphology for a) Reference HIPS, b) HIPS(SB/PS)R1 and HIPS(SB/PS)R2 (bar scale at 100 nm).

In the case of PB as the rubber, the phase inversion shifted to X=0.19 and the morphologies were of the Salami type (corroborated by TEM) and the salami morphologies increased their size (see Fig. 4) yielding materials with an increase in impact strength (from 60.14 J/m in the HIPS/PB to 77.36 J/m in the HIPS(PB/PS)) attributed to an increase in the interfacial tension between the phases.



Figure 4. Morphology for a) Reference HIPSPB (scale bar at 1micron) and b) HIPS(PB/PS) (scale bar at 0.5 micron).

## Conclusions

HIPS were successfully synthesized starting from a heterogeneous solution and the materials thus obtained presented higher impact strength than those obtained by the traditional method (homogeneous solution). Also, it was elucidated on the haste with which the inversion phase takes place and the morphological development in such heterogeneous systems, giving light to the implementation of a new strategy to significantly increase the particle size and therefore, to increase the impact resistance of these materials.

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# DESIGN OF A LITHIUM-ION BATTERY USING POLYSULFOBETAINES AS ELECTROLYTIC SUPPORT

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#### Abstract

Lithium ion batteries constructed using cobalt spinel (LiCoO2) as cathode and lithium disc as anode are characterized when polysulfobetaines are used as electrolytic support and separator. The ionic conductivity of these polysulfobetaines has been previously determined in a cell with blocking electrodes. The ion lithium cell voltage was 2.8 V when a Poly(methacrylate sulfobetaine mixed with LiClO4, or LiClPF6 1:1 mol were used as electrolyte. After five charge-discharge cycles, the voltage value diminished to 2.1 V. Since the polysulfobetaine has a  $Tg=18^{\circ}C$  the material presents a rubbery consistency which is not self-supported. Different polymer films were used as electrode separator; however, the cell voltage was low. At the moment, the polymer synthesis is being optimized in order to use polypropylene-supported polysulfobetaine

#### Introduction

The rechargeable Li batteries offer the highest energy density of any battery technology, and they power most of today's portable electronics. In the design of a lithium-ion battery the electrode selection is important as well as the selection of the electrolyte and electrolytic support. In the commercial batteries of this kind -like those used in laptops- the cobalt spinel (LiCoO2) or manganese spinel (LiMnO2) are used as cathode. For the anode, conductive graphite (SUPER P ®) agglutinated with polyvinylidene fluoride (PVDF) or lithium disc are used. A solution of LiPF6 in propylene and ethylene carbonates embedded in highly porous microfiber is used as electrolyte and separator between anode and cathode. These electrolytes have shown different problems during the battery operation specially associated to the high flammability and reactivity in front of the electrode materials. Some alternatives have been proposed to avoid these problems, as zwitterionic polymers.

The synthesis, structure and dielectric properties of zwitterionic polymers have been extensively studied [1,2]. These polymers have shown interesting properties; particularly those related to electrical conductivity and associated phenomena. Their applications in the production of solid-state batteries are potentially suitable. In the absence of salts, the presence of zwitterionic structures of two opposed sign charges joined by covalent bonds provides specific dipole-dipole interactions, which induce conductivity levels comparable to those of salt-polyether systems. In this work, we present the possible use of polysulfobetaines as electrolytic support and separator for a lithium-ion battery.

#### Experimental Synthesis of PMBS-4

PMBS-4 was synthesized according to Cardoso et al. [1]. Bulk polymerization was carried out at 60°C, 50 mmHg for 24 h. ACVA was used as radical initiator. The polymer was washed twice with ethanol. The polymer was dissolved in trifluoroethanol, precipitated in cold acetone, and dried in a vacuum oven at 50 °C for 48 h.

PMBS-4 and LiClO<sub>4</sub>, or LiClPF<sub>6</sub> (Aldrich Chemical Co.) 1:1 mol were dissolved in trifluoroethanol. The solution was continuously stirred for 24 h at room temperature or until the solution looked homogeneous and then dropped into a circular Teflon mold. Residual solvent was slowly evaporated. The samples ware kept in a desiccator until their further use. These systems were labeled PMBS-4/LiClO4, and PMBS-4/LiPF6.

## **Polymer Characterization**

PMBS-4 structure was verified by <sup>1</sup>HNMR in a 5-10% weight solution of D2O with 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt as an internal reference.  $\delta$  units were polymers Thermogravimetric measurements were performed with a PIRYS Perkin Elmer under a 50 cm3/min nitrogen flow. Differential scanning calorimetry was carried out under a nitrogen flow (50 cm3/min) with a MDSC2920 Modulated Differential Scanning Calorimeter manufactured by TA Instruments (Newcastle, Delaware, USA). Modulated DSC scans were carried out at 5 °C/min with amplitude of  $\pm$  0.5°C and a period of 40 seconds within the ange of -50 to 180°C at a heating rate of 10 °C/min under 50 ml/min of nitrogen within the range of 30 to 500°C. The Tg reported of sample was obtained of the 2nd or 3rd scan, previous heating at 100°C and further isothermic process at 100 °C for 180 min to eliminate the maximum water absorbed on the sample.

# Swagelok-type cell design

The cell design was established according to Beattie et al's work [3] (see Figure 1). For the anode, conductive graphite (SUPER P ®) agglutinated with polyvinylidene fluoride (PVDF) is used or disks 3/8 in. diameter of lithium (Sigma Aldrich, 99.9%), with 0.38 mm thick and a solution of LiPF6 in propylene carbonate and ethylene carbonate as electrolyte. As cathode, LiCoO2 agglutinated with PTFE was used. Highly porous micro fiber was used as separator between the electrodes. Polysulfobetaine (PMBS-4) also was used as electrolytic support and separator. The Swagelok-type cells were assembled in an argon atmosphere glove box.

Determination Ionic conductivy of sulfobetaines.

After synthesis, the samples were put in a desiccator until the electrochemical measurements were carried out. This was done in order to prevent the humidity of air, since residual water in the electrolytes would greatly affect the ionic conductivity of the electrolytes. For impedance measurements, the samples (0.7 cm in diameter and 0.08 cm thick) were sandwiched between stainless steel electrodes using a two-electrode configuration. The samples were dried overnight in a hermetic cell, under Argon atmosphere and silica gel as desiccant agent. The impedance measurements of PMBS-4 plus LiClO4 or LiPF6 were carried out in a VMP3 - MultiPotentiostat/Galvanostat from Biologic Science Instruments, in the frequency range of 1 MHz - 10 mHz. Temperature was controlled in the cell and the range covered was from 25° to 80 °C.

Lithium battery tests. The cycling character of the battery was evaluated in laboratory as follows: Li/1 M LiPF6 in PC:DEC (1:1 in weight ratio)/LiCoO2, Super P black carbon: where PC= propylene carbonate, DEC=diethyl carbonate.



Figure 1. Swagelok-type cells

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#### **Results and Discussion**

Table I shows the polymerization conditions and the elemental analysis results, which confirm the proposed structure presented in Figure 2.

Sample	[MBS]	%C		%H		% N		%S	
	[I]	Theo	. Exp.	The	o. Exp.	The	eo. Exp.	Theo	o. Exp.
PMBS-4	500	40.9	41.4±0.5	9.2	8.2±0.5	2.4	$2.2\pm0.5$	7.0	8.09±0.5

Table I. Synthesis conditions and Elemental Analysis results

a PMBS-4 sample was analyzed twice and corrected for water content according to TGA result



Figure 2. Structure of PMBS-4

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were used to determine the glass transition temperatures (Tg) and thermal stability of the polymers. Tg values are found and disclosed in Table II. The presence of  $Li^+$  ions in the PMBS-4 polymer causes that the Tg remains almost unchanged, while the temperature range along which the heat capacity changes is broader. Percent humidity and the initial decomposition temperature (Td<sub>i</sub>) for each sample are also reported in Table II. Thermally stable polymers are sought for applications in battery devices, and in this regard, PMBS-4/LiClO<sub>4</sub> shows the highest degradation temperature (187°C).

Table II. Thermal Properties. Glass Transition Temperature (Tg), temperature range of the Tg event  $(\Delta T)$ Tg, and Initial Decomposition Temperature (Tdi)

System	Tg (°C)	$(\Delta T)Tg(^{\circ}C)$	%H <sub>2</sub> O	Td <sub>i</sub> (°C)
PMBS-4	19±1	17-22	14±2	160±1
PMBS-4/LiClO <sub>4</sub>	31±1	29-31	14±2	187±1
PMBS-4/LiPF <sub>6</sub>	33±1	20-29	13±2	177±1

#### **Impedance Measurements**

In order to obtain the values of conductivity of PMBS-4 samples, several sets of measurements were performed using EIS. The measurements were carried out in the frequency range of 1MHz–10 mHz, at the open circuit potential, and different temperatures. The Cole-Cole spectra of PMBS-4/LiClO4 and PMBS-4/LiPF6 are shown in Figure 3a and 3b respectively. In all cases, the spectra show two partial semicircles. The first one appears at high frequencies, while the second one at middle to low frequencies. The depressed semicircle, in the higher frequency range, is associated to the ionic resistance (Rb) and the bulk properties of the polymer electrolyte (PMBS-4), at lower frequencies the partial semicircle is the typical response of blocking electrodes [4, 5]. The ionic resistance (Rb) of the polymer electrolyte can be readily obtained by using the electrical circuit in Figure 3c. In this electric circuit Rb represents the resistance of the solid polymeric electrolyte (SPE), Ri is the resistance of SPE/stainless steel electrode interface; the impedance of CPE is defined as ZCPE =1/[ (jw)n Qb], where:  $j = \sqrt{-1}$ , w is the angular frequency, nb takes into account

the inhomogeneity of the system (roughness, porosity). CPEb is associated to the bulk properties of- the SPE. Ci is associated to the space charge capacitance of the stainless steel electrode. The Cole-Cole plots of PMBS-4 samples were analyzed using the electric circuit in Figure 3c and Zview® as fitting program. The electric circuit allowed a good fit ( $\chi \sim 10^{-3} - 10^{-4}$ ) to experimental impedance spectra. Ionic conduction inside the SPE comprises complex mechanisms and different interactions such as ion-PMBS-4 (due to the zwitterionic nature of PMBS-4, see Figure 2) and Li+- Li+ interactions within the SPE, therefore Rb is related to the resistance of ion transportation within the SPE. All these interactions are responsible for the depressed and incomplete semicircles observed in the high-frequency range in Figure 3.



Figure 3. Cole-Cole plots of : a) PMBS-4/LiClO<sub>4</sub>, b) PMBS-4/LiPF<sub>6</sub> and c) Electric circuit used for analyzing the Cole-Cole spectra. Spectra were acquired at different temperatures: i)  $25^{\circ}$ C, ii)  $40^{\circ}$ C, iii)  $60^{\circ}$ C and iv)  $80^{\circ}$ C. Spectra in continuous line belong to calculated spectra using the best-fit values obtained from the fitting procedure and the electric circuit.

The Rb values are inversely related to the ionic conductivity  $\sigma$  of the SPE, according to equation 1

$$\sigma = \frac{l}{AR_b} \tag{1}$$

where: *l* is the thickness of the SPE and A is its geometrical area.

The plots of Log  $\sigma$  vs. T of the different samples are shown in Figure 4; the plots indicate an Arrhenius behavior for all the samples. The equation  $\sigma = \sigma_0 e^{-Ea/kT}$  (where  $\sigma_0$  is a pre-exponential factor, Ea is the apparent activation energy, k is the Boltzmann constant and T is the absolute temperature) approximates fairly well its behavior. The conductivity values at 25°C and the bulk activation energy calculated from this equation are reported in Table III. The increase in conductivity with increasing temperature can be explained as a hopping mechanism between coordinating sites, local structural relaxation and segmental motion of polymer. Above Tg, the amorphous region is present and ion mobility is largely enhanced by segmental motion of more flexible polymer chains. With increasing temperature, the conductivity increased for all samples over the full range of measured temperatures because the improved segmental movement of polymer chains was more favorable to enhance ion mobility and conduction. In Table III, the conductivity values, at 25°C, of PMBS-4 complexes, follow the order PMBS-4/LiPF<sub>6</sub> > PMBS- $4/LiClO_4$ . Contrary to this, the values of Ea follow the order PMBS- $4/LiPF_6 < PMBS-4/LiClO_4$ . By considering that Li+ conductivity follows a hopping mechanism within the PMBS-4, the hop of Li<sup>+</sup> toward another equivalent site requires certain activation energy. However, for each positive charge transported in a certain direction, a negative charge must balance out in order to preserve electroneutrality; thus, negative charges must be able to move. The latter means that the counterion of the lithium salt plays a major role in the value of conductivity, and seems to indicate that PF6- has a weaker interaction with the zwitterionic structure of PMBS-4 than ClO4- does; however, more experimentation is needed in order to confirm this hypothesis.



Figure 4. Arrhenius plots of: i) PMBS-4, ii) PMBS-4/LiClO4, iii) PMBS-4/LiPF6.

Toble III 1	onia conductivities	$(\boldsymbol{\sigma})$ of	25°C and active	tion on array (	$\mathbf{E}_{0}$ of $\mathbf{D}_{0}$	IDS 1 complex
Table III. I	ionic conductivities	$(\sigma)$ at	$25^{\circ}$ C and active	ation energy (	Ea) of PN	1BS-4 samples.

Sample	$\sigma 25^{\circ} C (S/cm)$	Ea (eV)
PMBS-4	1.02E-06	0.67
PMBS-4/LiClO4	2.09E-05	0.81
PMBS-4/LiPF6	8.57E-05	0.57

#### PMBS-4 as electrolyte support

Use of PMBS-4 as solid electrolyte and separator in Li-ion batteries is viable. Open circuit voltage of 2.8 V vs. Li<sup>o</sup>/Li+ has been obtained. The operational voltage for the charge process is around 3.6 V vs. Li<sup>o</sup>/Li+. It had obtained large resistances; furthermore the ohmic drop must be measured experimentally. Efforts to optimize electrical and ionic conductivity through the cell are currently underway.

#### Conclusions

A polymer of the zwitterionic type was synthesized and characterized. Its thermal, conductive and electric properties were studied in detail. Conductivity of all the analyzed samples changed with temperature, following an Arrhenius-like behavior. It is proposed that the conductivity observed in PMBS-4 is caused by the dipoles within the zwitterionic material. Conductivity of SPE decreases as follows: PMBS-4/LiPF<sub>6</sub> > PMBS-4/LiClO<sub>4</sub> > PMBS-4. The ionic conductivity of these materials is mainly due to Li+; however, the anion of Li salt clearly affects the ionic conductivity of SPE

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# SYNTHESIS OF AN INTERPENETRATED NETWORK POLYMER AS COMPATIBILIZER FOR RECYCLED PET AND LDPE.

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In order to improve mechanical and thermal properties of recycled poly (ethylene terephtalate) (PET)/polyethylene of low density (LDPE) blends [1,2], an Interpenetrated Network Polymer, based on ABA type thermoplastic elastomer and poly (acrylic acid), was synthesized and used as compatibilizer of these plastics, which are two of the most generated plastic waste [3].

The effect of concentration of compatibilizer in the blend PET / LDPE, at 1 and 5% w/w, and the relative amount of poly (acrylic acid) in the compatibilizer, from 70 to 90% w/w, were evaluated. The blends were processed using a twin-screw extruder and the obtained samples were characterized by infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), scanning electron microscopy (SEM) and stress-elongation tests. The results show that the new compatibilized material obtained has better properties with respect to its parent material with changes in morphology, mechanical and thermal behavior depending on the content of poly (acrylic acid) and the compatibilizer content. The less poly(acrylic acid) content in the compatibilizer the higher modulus for the blend of PET/LDPE with a ratio of 75/25. In addition, there is an slight effect of the concentration of compatibilizer on blend in the stress-strain characterization when there is a low quantity of PET in the blend (25 %) but have a dramatic effect when the PET content was increased (75% w/w).

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# SYNTHESIS OF POLYMERIC MATERIALS FROM NOPAL MUCILAGE AND GLYCEROL DOPED WITH SILVER NANOPARTICLES

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#### Abstract

Nopal (Opuntia ficus-indica) mucilage has been used as a natural polymeric material with applications in water treatment for clarification and/or removal of heavy metals, as well as a raw material to develop edible plastic film. Mucilage contains carboxylic acids that are potentially capable of reacting with hydroxyl groups, and therefore, this material should be able to form polyester.

Polymeric materials were synthesized from nopal mucilage, oxalic acid or citric acid, and glycerol containing dispersed nanometer-sized particles of silver. Two different ratios of glycerol to oxalic/citric acid were used. The synthesized materials were characterized by infrared spectroscopy (FTIR-ATR) and swelling. Depending on the ratio of glycerol/oxalic (or citric) acid, the synthesis leads to both rigid and flexible polyesters. Infrared spectroscopy identified saturated carboxylic acids, hydroxyl groups and esters, confirming the reaction between the nopal's carboxylic groups, oxalic (or citric) acid and the hydroxyl groups of glycerol.

The synthesized polymers showed different capacities to absorb water. The mucilage sample with glycerol but without oxalic acid had a greater absorption capacity (836%) but lacked mechanical properties. The mucilage sample with glycerol and oxalic acid showed lower absorption capacities (474%) and better mechanical strengths, due to crosslinking role of the carboxylic acid.

#### Introduction

Nopal is found naturally in arid and semiarid regions in many countries, including Mexico and the United States. It is a plant that can survive in extreme temperatures and drought. In addition, have a great capacity to store water in through the mucilage content in tissue (1)

The cactus mucilage is a natural polymer (2) which is composed of the average sugar composition of the mucilage from O. ficus indica cladodes added up to 42% arabinosa, 22% xylose, 21% galactose, 8% galacturonic acid, and 7% rhamnose. Precipitation is achieved by cation addition of calcium, lead, barium, silver, copper, iron, cobalt, or nickel (3).

For centuries, mucilage has been used as a flocculant in water turbidity for natural spring water. (4). Recently, it has been investigated about its ability to remove heavy metals from water. The mucilage extract particulate settling rates shows an increment of 330% compared to a commonly flocculants, like aluminum sulfate, at dosage concentration of 3 mg / 1. Flocculation performance of mucilage is equivalent to aluminum sulfate at doses 0.3% of the aluminum sulfate concentration required.

In addition, Opuntia ficus indica mucilage has the ability to form edible films at pHs between 4 and 8. Without plasticizer, films are rigid and very fragile, so it is necessary to add a plasticizer to improve the elastic properties of the film. The possible formation of intramolecular links of calcium with carboxylic groups of the mucilage`s molecule causes an adverse effect on the water vapor permeability (WVP), as well as on the tensile strength, while improving the elongation percentage of the films. The elevated WVP of the mucilage films can be attributed to its

hydrophilic property (5).

It is important to point out that it has not investigated the use of other compounds to form a solid network insoluble in water from nopal mucilage.

The carboxylic acid groups have a tendency to donate their H ion, and they are able to react with R'OH to generate ester group. The primary R'OH groups are more labile than secondary or tertiary groups. Also, they can react with amine groups to gives amide functionality.

Silver nanoparticles have chemical and biological properties that are appealing for consumer products, food technology, textiles/fabrics, and medical industries. Nanosilver also has unique optical and physical properties that are not present in bulk silver, and which are claimed to have great potential for medical applications.

Nanosilver is an effective anti-microbial agent against a broad spectrum of Gram-negative and Gram-positive bacteria (6,7), including antibiotic-resistant strains (8). Gram-negative bacteria include genera such as Acinetobacter, Escherichia, Pseudomonas, Salmonella, and Vibrio. A cinetobacter species are associated with nosocomial infections, is reasonable to suggest that the resultant structural change in the cell membrane could cause an increase in cell permeability, leading to an uncontrolled transport through the cytoplasmic membrane, and ultimately cell death, (9),

In addition, silver nanopaerticles are an effective, fast-acting fungicide against a broad spectrum of common fungi including genera such as Aspergillus, Candida, and Saccharomyces (10). The exact mechanisms of action of silver nanoparticles against fungi are still not clear.

# Experimental

# Extraction and precipitation of the mucilage

Mucilage extraction was carried out as follows. Nopal cladodes were crushed and boiled with destilled water, at 90 C during 60 min. Then, the mixture was filtered to separate the fibrous material of mucilage. The liquid extract was precitated with acetone. After the precipitation, the obtained material was dried at 60 C for 48hrs, then was pulverized and placed in a desiccator.

# Film preparation

The films were prepared by solubilizing the mucilage in 20 ml of distilled water at room temperature for 6 hrs with constant stirring. After this, the oxalic (or citric) acid was added and then the silver nanoparticles also were added to the mucilage solution. At 1 minute and 6 minute, it was added 0.01 ml of 0.1N sulfuric acid as catalyst, and solution was stirred to complete 1 hour. The mixture was poured on Teflon plates and dried for 48hrs at 60 C.

The film preparation was carried out by a design of experiments.

# Swelling tests

For the swelling test, a small quantity of the film was immersed in distilled water, and the weight was recorded at several times from 0 to 120 minutes. Initial weight (Wi), final weight (Wf). The % swelling was calculated from:

% swelling = 
$$\frac{Wf - Wi}{Wi} \times 100$$

Point of zero charge (PZC)

The point of zero charge, it was carried out placing a 20 mg piece of film into 3 ml of deionized water in sealed tubes under constant stirring during 3 days and then, once the equilibrium was considered that was reached, the pH of the solution was recorded.

# FTIR

The FTIR analysis was carried out using a FTIR Nicolet-1700 spectrometer with an ATR additament. The wavelength was from 4000 a 550 cm-1 with 64 scans. The sample was not treated previous to characterization.

## **Results and Discussion**

The obtained results are summarized in Tables 1 and 2. In the first case (Table 1) the results correspond to those obtained when oxalic acid was used. Table 2 shows the obtained results using citric acid.

sample	temperature	Mucilage, g	oxalic acid, g	Ag, g	Swelling %	PZC
1	25	0.5	0.5	0	215.0684932	1.6
2	70	0.58333	0.333333	0.083333	147.5247525	1.68
3	70	0.83333	0.083333	0.083333	196.1538462	3.17
4	70	0.66667	0.166667	0.166667	100	3.01
5	70	0.5	0.5	0	117.4603175	1.57
6	25	0.66667	0.166667	0.166667	119.8347107	2.48
7	25	0.5	0	0.5	608.3333333	6.65
8	25	0.58333	0.083333	0.333333	283.2335329	2.99
9	70	0.58333	0.083333	0.333333	438.21	2.69
10	70	0.5	0	0.5	1652.11	4.86
11	70	1	0	0	2105.9	6.31
12	25	0.83333	0.083333	0.083333	410.79	2.82
13	25	0.58333	0.333333	0.083333	194.87	4.35
14	25	1	0	0	3497.4	6.5

Table 1. Results using oxalic acid

In table 1 shows that the sample which does not contain oxalic acid has an increased swelling, probably due to mucilage is not crosslinked. In addition, it is noted that there is an effect of the temperature on swelling. Thus, the higher the temperature the higher swelling capacity, since the reaction temperature could accelerate the crosslinking reaction. The mixtures without oxalic acid are solubilized in water quickly.

sample	temperature	Mucilage, g	citric acid, g	Ag, g	Swelling %	PZC
1	25	0.5	0.5	0	623.36	2.86
2	70	0.58333	0.333333	0.083333	528.23	3.2
3	70	0.83333	0.083333	0.083333	1391.7671	4.44
4	70	0.66667	0.166667	0.166667	139	3.61
5	70	0.5	0.5	0	254.62	2.58

Table 2. Results using citric acid

In table 2 it can be seen that with citric acid yields a higher percentage of swelling, as well as increased PZC, respect to the samples obtained with oxalic acid and similar reaction conditions. Thus, it is possible to say that citric acid could give a tridimensional network (since it has 3 hydroxyl groups), which gives a higher crosslinked material compared with the obtained material with oxalic acid. FTIR

The Figure 1 shows the spectra of mucilage, oxalic acid and the corresponding obtained material.



Figure 1. Spectra of parent material and product. Groups: 1 OH, 2 carboxylic acid, 3 tertiary alcohol, 4 Aldehyde, 5 primary amines, 6 amides





Figure 2. Spectra of parent material and product. Groups: 1 OH, 2 carboxylic acid, 3 tertiary alcohol, 4 Aldehyde, 5 primary amines, 6 amides

The analysis with FTIR shows that the mucilage fraction obtained has a composition similar to that of commercial pectin (spectrum not shown). The representative functional groups found are OH, aldehides, primary amines and amides. In samples of the synthesized material shows a

change in signal intensity, possible due to chemical interaction between molecules. For example, there was an increase in the peak of amides, so possible the OH of the carboxylic acid reacts with the amino groups of the mucilage, but still not clear what is the interaction between polymer molecules and the carboxylic acid.

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## STUDY OF CHITOSAN- GLUTARALDEHYDE-XANTHAN HYDROGEL LIKE ADSORBENT OF CADMIUM (II)

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Rapid industrialization has led to increased disposal of heavy metals into the environment. The heavy metals removal of water bodies by means of adsorption constitutes a form of remediation of the pollution [1-4]. To determine the behavior of the synthesized hydrogel based on chitosanxanthan gum and crosslinked with glutaraldehyde as adsorbent of Cd (II) in watery solution, kinetic studies were made in a batch system at three temperatures (25, 30 and 35 °C) and two concentrations (10 and 20 mg/L) at pH 6.5 to avoid precipitation of the metal. In results was observed that the adsorption process was carried out quickly the first 60 minutes and equilibrium was reached after 120 minutes. The maximum removal of metal ions was obtained at a temperature of 35 °C when the initial concentration was 10 mg/L. Adsorption kinetics data were fit to pseudo first and pseudo second order models, experimental data fitted better to the pseudo second order model so that it can be assumed that the limiting of the process is chemical adsorption. In what concerns the studies of equilibrium of adsorption, three experiments were carried out varying the metal concentration (1-20 mg/L) and temperature (25, 30 and 35 ° C), with a contact time of 120 minutes, comparing experimental data with two adsorption isotherms showed that Langmuir isotherm displayed a better fitting model than Freundlich isotherm on the adsorption of Cd (II) onto the hydrogel.

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## MODELING OF NETWORK FORMATION IN REVERSIBLE-DEACTIVATION RADICAL COPOLYMERIZATION OF VINYL/DIVINYL MONOMERS USING A MULTIFUNCTIONAL POLYMER MOLECULE APPROACH: ATRP, NMRP AND RAFT CHEMISTRIES

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Reversible-deactivation radical polymerization techniques, which are important methods for obtaining well-defined, low dispersity polymers[1], have also shown to be useful tools for the synthesis of polymer networks with reduced heterogeneity[2,3]. In this contribution, a new mathematical model for the kinetics of reversible-deactivation radical copolymerization with crosslinking of vinyl/divinyl monomers is presented. The cases of NMRP, ATRP and RAFT were investigated. With the aim of correctly describing the kinetics of network formation, a reaction scheme considering multifunctional polymer molecules was proposed and therefore, a single mass balance equation for polymer species was required. For NMRP and ATRP, a three-dimensional mass balance equation was enough for describing the kinetics, whereas for RAFT polymerization, a penta-dimensional mass balance was needed. In order to simplify the mathematical treatment of the copolymerization reaction, the "pseudo-kinetic rate constants method" was used. Average properties of the multidimensional distribution were calculated using the method of moments. Flory-Stockmayer's theory was used for calculating average molecular weights during post-gelation period. Polymerization rate, molecular weight development, gelation point, gel content, crosslink and cyclization densities, copolymer composition and concentrations of the different species involved in the polymerization mechanism can be calculated with the model. The model was validated using experimental data reported in the literature. Several conditions for the three types of reversible-deactivation processes were examined, showing good agreement in all cases. It was found that the presence of a reversible-deactivation reagent has an important effect on the kinetics of network formation, delaying the gelation point and reducing the cyclization rate. According to the results, overall monomer concentration, controller/initiator ratio and crosslinker initial concentration are the governing factors for the development of average crosslink and cyclization densities and, therefore, for the homogeneity of the resulting polymer network.

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- [3]. Ide N., Fukuda, T., *Macromolecules* 32, 95-99 (1999)
# COPOLIMERIZATION KINETICS OF STYRENE AND DIVINYLBENZENE IN THE PRESENCE OF S-THIOBENZOYL THIOGLYCOLIC ACID AS RAFT AGENT

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## Abstract

An experimental study on the kinetics of the reversible addition-fragmentation chain transfer (RAFT) copolymerization of styrene (STY) and divinylbenzene (DVB) is presented. The experiments were carried out in bulk from a mixture of monomers, S-thiobenzoyl thioglycolic acid, used as RAFT agent, and initiator (dibenzoyl peroxide, BPO), at 80°C. The effect of RAFT agent concentration, including the case without RAFT controller, on polymerization rate, molecular weight development, gel fraction, and swelling index was analyzed.

## Introduction

Crosslinked polymers (polymer networks) are used in many technological areas of great importance for the human being. Polymer networks are used as paints, construction materials, coatings, polymer glasses with high mechanical strength and high thermal stability, superabsorbent materials, food packaging, implants, controlled drug-release matrices and artificial organs [1-4], to name a few applications.

Poly(styrene-co-divinylbenzene) is a crosslinked polymer with attractive properties. It has an excellent stability at high temperatures and under physical stresses. It is dimensionally stable under a wide variety of conditions, due to its rigid network structure. It finds applications in chromatographic columns, exchange resins [5–8] and enzyme immobilization [9] and can be used at a wide range of pHs. It is possible to modify its surface so that it can be used as a catalytic support and for other applications [10].

Controlled/"Living" radical polymerization (CLRP) processes have allowed the synthesis of polymer materials with controlled microstructures which find uses in technologically important areas, such as aerospace, nanotechnology, industrial electronics, and biomaterials [9–13]. Reversible addition-fragmentation transfer (RAFT) polymerization has proven to be one of the most effective CLRP processes because of its advantages over other CLRP techniques (atom-transfer radical polymerization, ATRP, and nitroxide-mediated radical polymerization, NMRP), such as the applicability of the technique to a larger range of monomer types, reaction conditions (temperature and pressure), and processes (homogeneous and heterogeneous) [14, 15].

Most applications of polymer networks require homogeneous structures to obtain optimal performance. However, polymer networks obtained by free-radical copolymerization of vinyl/divinyl monomers are heterogeneous in nature. It would be desirable to have a synthetic route to synthesize homogeneous polymer networks using free radical technology. This goal may be possible to achieve by copolymerizing vinyl and divinyl monomers in the presence of CRP controllers [6].

The production of polymer networks by controlled/"living" radical copolymerization (CLRC) techniques, including the copolymerization of vinyl/divinyl monomers, has already been addressed in the open literature for the cases of INIFERTER, ATRP, NMRP and RAFT. A short review of these studies is offered in Hernández-Ortíz et al. [16].

# Experimental

## Reagents

Styrene (STY; 99%, Aldrich) was washed with a 5-wt% NaOH solution, dried with magnesium sulfate, and distilled under vacuum at 22 °C. Divinylbenzene (DVB; 80 %, Aldrich) was a mixture of isomers with 80wt% of 1,3- and 1,4-DVB and 20wt% of 1,3- and 1,4-ethylvinylbenzene (1,4-EVB). BPO (97 %, Aldrich) was used as initiator and S-thiobenzoyl thioglycolic acid (99 %, Aldrich) as RAFT agent. DVB, BPO, and the RAFT agent were used as received.

## **Polymerization System**

The copolymerizations were carried out in sealed ampoules of 5mm inner diameter and approximately 25 cm in length. Solutions were prepared with the appropriate amounts of STY, DVB, BPO, and the RAFT agent, according to the recipes described in Table 1. Aliquots of the solution were then transferred into the ampoules. The contents of the ampoules were degassed by three successive freeze-thaw cycles under vacuum. The ampoules were torch-sealed under vacuum and then placed in liquid nitrogen until used. The polymerizations were initiated by immersing the ampoules in a programmable bath with temperature control, containing silicon oil at 80 °C and then stopped at the desired times by inserting the ampoules into frozen water. Once the ampoules were opened by using a glass cutter, the reaction mixture was transferred into a flask with dichloromethane, containing hydroquinone to inhibit further reaction. After dissolving in dichloromethane, the polymer was precipitated with methanol, left in air flow for two days, and then dried in a vacuum oven until constant weight was obtained.

Run	Monomer	DVB, wt%	BPO, wt%	[RAFT]/[BPO]
1	STY/DVB	1	1	0
2	STY/DVB	1	1	0.7
3	STY/DVB	1	1	1
4	STY/DVB	1	1	1.5

 Table 1. Experimental scheme. \*

\*All reactions were conduced at 80°C.

# **Polymer Characterization**

Monomer conversion was measured gravimetrically. Gel content and swelling index (SI) were determined gravimetrically from fractions separated by ultracentrifugation. A Beckman centrifuge (Optima XL- 100 K, class H) with a fixed angle rotor and 60 000 rpm maximum was used. The samples were centrifuged at 18 000 rpm for 1 h. Molecular weight averages of the soluble fraction were determined by size exclusion chromatography (gel permeation chromatography, GPC). The GPC equipment consisted of a Waters Alliance 2695 with Waters 2414 refractive index, a Viscotek viscometer (model 270), and Waters 2996 UV detectors. Four columns (Shodex KF802, KF803, KF804, and KF806) in series were used in the setup. Tetrahydrofuran (THF; >99.9 %, Aldrich) was filtered and taken as eluent at a flow rate of 1mL min–1. For both setups, polymer solutions of about 0.25 wt% were prepared and left for 24 h to fully dissolve the polymer. The solutions were microfiltrated. Injection volumes varied from 100 to 200 IL.

#### **Results and Discussion**

Figure 1 shows the effect of the controller-to-initiator ratio on the polymerization rate, expressed as conversion versus time. As expected, due to the retardation effect in RAFT polymerizations [14, 15], the polymerization rate decreases as the controller concentration is increased. Full conversion is achieved within about 8 h for the case without controller whereas almost 70 h are needed to reach 70% monomer conversion for the case with the highest controller content (RAFT/BPO = 1.5).



**Figure 1.** Effect of the RAFT/BPO molar ratio on monomer conversion versus time in the RAFT copolymerization of STY/DVB under the conditions of Tab. 1 and T = 80 °C.



**Figure 2.** Effect of the RAFT/BPO molar ratio on Mn and Mw development in the RAFT copolymerization of STY/DVB under the conditions of Tab. 1 and T = 80 °C. (a) Combined cases, (b) RAFT/BPO = 0, (c) RAFT/BPO = 0.7, (d) RAFT/BPO = 1, (e) RAFT/BPO = 1.5.

The molecular weight development for the four cases studied in this paper is demonstrated in Figure 2; it is observed that the gelation point is delayed as the amount of RAFT controller is increased. The gelation point seems to occur at approximately 20, 40, 65, and later than 70% (not observed in the range studied) monomer conversions for the cases with RAFT/BPO = 0, 0.7, 1, and 1.5, respectively.

The delay in the gelation point is caused by the fact that chains of shorter sizes are obtained in controlled systems due to the reduced concentration of polymer radicals, thus taking longer to reach the point of infinite size. This behavior suggests that more homogeneous polymer networks than in conventional vinyl/divinyl copolymerization are possible, at least in the case with the highest controller content.



**Figure 3.** Effect of the RAFT/BPO molar ratio on the gel fraction versus conversion profile for the RAFT copolymerization of STY/DVB under the conditions of Tab. 1 and T = 80 °C. Trends shown as solid lines.

The steep consumption of the sol phase (steep growth of the gel phase) for the cases without controller and for the cases with RAFT/BPO = 0.7 and 1 is clearly observed in Figure 3. The gelation point occurs at approximately 10-20, 35-45, and 50-65% monomer conversion for the cases with RAFT/BPO = 0, 0.7, and 1, respectively. Although not shown, gel content determination was also carried out for the case with RAFT/BPO = 1.5. Considering the experimental error, the results obtained showed that there is no gel formation for that case in the range studied (conversion lower than 70 %, due to the very slow polymerization rates obtained under these conditions).

## Conclusions

An experimental kinetic study the copolymerization with crosslinking on of styrene/divinylbenzene in the presence of S-Thiobenzoyl thioglycolic acid as RAFT agent was presented. It was confirmed that the addition of a RAFT controller delays the gelation point. The fact that lower Mw values during the pregelation and higher degrees of swelling were obtained in the controlled cases suggest that the molecular weight distribution of the connecting primary chains between crosslinkages is more homogeneous and it is likely that the crosslink density distribution are also more homogeneous in these controlled cases.

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# ELECTROPOLYMERIZATION AND ELECTROCHROMIC CHARACTERIZATION OF POLYANILINE FILMS

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## Abstract

Conducting

Conducting polyaniline (PANI) has been electrochemically synthesized on FTO-coated glass. The PANI films were grown at constant potentials and characterized by cyclic voltammetery (CV), UV-visible spectrophotometry, spectral reflectance techniques and SEM. PANI films thicknesses were observed in the range of 60 to 250 nm. PANI films showed optical attenuations in the range of 11% to 42% at the wavelength of 650 nm (red color) and in the range of 14% to 53% at infrared wavelengths. The maximum contrast was archived by potentiodynamic deposition at a scan rate of 100 mV/s. In this case, the surface concentration of the charge carrier species was estimated to be  $7.7 \times 10^{-7}$  mol cm<sup>-2</sup>, while the charge carrier mobility obtained was  $\sim 3.6 \times 10^{-9}$  cm<sup>2</sup> s<sup>-1</sup> which result in its having a high coloration efficiency (>50 cm<sup>2</sup> C<sup>-1</sup>).

## Introduction

Conductive conjugated polymers show a great versatility in its application of technology: can be used as electrodes in batteries, in microelectronics, material sensors, electrochromic devices and as support for catalysts in cells fuel, among others. Particularly polyaniline (PANI) has been the subject of numerous investigations, due to their ease of synthesis, electrochemical stability and conductivity In this work, PANI thin films are evaluated with the aim of to build electrochromic devices.

Aniline (amino benzene) is a organic compound with chemical formula  $C_6H_5NH_2$ . Its aromatic ring, specifically their double bonds, provided a cloud of electrons, with which around the nitrogen, make this polymer an electronic conductive element. Polyaniline (PANI) has the general formula:

 $[(-B-NH-B-NH-)_x (-B-N=Q=N-)_{1-x}]_n$ 

In which B and Q correspond to compounds in the form  $C_6H_4$  benzene and quinone respectively.Parameter x varies between 0 (reduced PANI, poly-leucoemeraldine) and 1 (oxided PANI, poly-pernigraniline) and n is the degree of polymerization.

The electropolymerization can be carried accomplished in several ways: potentiodynamic, potentiostatic, galvanostatic and potentiostatic pulses. In this work potentiostatic technique are used.

## **Experimental setup**

Electrochemical oxidation was conducted in conventional three-electrode configuration. at ambient pressure and temperature, in a bath of 50 ml aqueous solution of 0.2 M of aniline and 1M  $H_2SO_4$ .

Homemade FTO coated glass (10 ohm/ $\Box$ ) were used as work electrode, while as auxiliary and reference electrodes were used platinum wires of 0.02cm diameter, bearing a counter in the effective surface of 0.1 cm<sup>2</sup>. All the potentials reported here are in reference to this electrode. After the deposition the films were washed in an ultrasonic bath in order to remove the film not polymerized over the substrate.

Polarization curves of PANI electropolymerization on FTO were made in order to identify formation potentials of different PANI oxidation states. PANI films were deposited at such potentials, as it is shown on Figure 1. In each case, the deposition time was 5 seconds. Table 1 shows a summary of conditions and SEM observations.



Figure 1. Polarization curves of deposition of PANI in FTO, and the potential used porpotentiostaticelectropolymerization.

	Conditions	Thickness	Morphology
		(nm)	
P1	229mV	60	none
P2	314mV	174	Stars like
P3	445mV	165	Rod like
P5	725mV	190	Flakes

Table 1.Summary of samples and SEM observations.

## **Results and Discussion**

## SEM observations.

Figure 2 shows the different films morphology obtained. Grains observed in Figure 2(a) correspond to FTO film, while in Figures 2(b) to 2(d) different PANI morphologies are observed. Figure 3 shows two thickness measurements.



**Figure 2**. SEM images for the surface of PANI electrodes with different electropolymerization potential. a) 229 mV, b) 314 mV, c) 445 mV and d) 725 mV



Figure 3. Cross-sectional SEM images for the thickness of PANI electrodes with different electropolymerization potential

#### **Electrochemical characterization**

CV characterization of the PANI films showed two distinct redox peaks (Figure 3(a)), which prove that the PANI film was electroactive and exhibited reversible electrochemistry. The first oxidation peak (Peak I) is the polyleucoemaraldine radical cation which is further oxidised at higher potential to polyemaraldine (Peak II). On the reverse scan, polyemaraldine is reduced first to the partly reduced polyemaraldine radical cation (Peak III), and then to fully reduced polyleucoemaraldine (Peak IV)

The surface concentration of the PANI film,  $\Gamma$  can be estimated from a plot of Ip against  $\upsilon$  in accordance with Brown–Anson model [1] using the equation:

$$\frac{I_p}{\upsilon} = \frac{n^2 F^2 A}{4RT} \Gamma \tag{1}$$

where *n* represents number of electrons transferred (2), F is the Faraday constant (96,584Cmol<sup>-1</sup>),  $\Gamma$  is the surface concentration of PANI film (mol cm<sup>2</sup>), A is the surface area of the electrode (0.8 cm<sup>2</sup>), v is the scan rate (V s.1), Ris the gas constant (8.314 J mol K-1), and T is the absolute temperature of the system (298 K). the Randel–Sev′cik equation was used to determine the rate of electron transport (i.e., diffusion coefficient of the electrons, D<sub>e</sub>):

$$\frac{I_p}{\nu^{1/2}} = 0.4463 \frac{(nF)^{3/2} A \Gamma}{L(RT)^{1/2}} D_e^{1/2}$$
(2)



where L (cm) is the film thickness. Table 2 shows the electrochemical measurements carried out.

Figure 4. Cyclic voltammograms of PANI: (a) general features and (b) at different scan rates. Inset shows the linear dependence of peak currents of anodic peak I on the scan rate

Sample	Redox	Qred/Qox	Concentration
	charge density	charge density	
	$(\text{mC cm}^{-2})$		
P1	27.85	.75	8.34 E-09
P2	31.11	.79	4.26 E-08
P3	40.75	.84	2.65 E-08
P4	35.8	.92	5.32 E-07
P5	57.36	.89	6.73 E-07

#### Table 2. Electrochemical measurements.

#### **Electrochromic properties**

Electrochromic properties of the polyaniline films were compared by performing cyclovoltammetry, optical transmittance spectroscopy, and measurement of coloration contrast at a fixed wavelength (650 nm). Transmittance spectra were recorded for as deposited, colored, and bleached films. The coloration efficiency at efficiency at the maximum contrast wavelength, 650 nm (red color), was calculated as

$$\eta_{650} = \frac{\Delta OD_{650}}{Q} \tag{3}$$

Where Q is the injected charge per unit area, and  $\Delta OD_{650}$  is the change in optical density at 650 nm defined by

$$\Delta OD_{\lambda} = \ln \left( \frac{T_{b\lambda}}{T_{c\lambda}} \right) \tag{4}$$

Where  $T_{b\lambda}$  and  $T_{c\lambda}$  are the simple transmittances in the bleached and colored states respectively, at wavelength  $\lambda$ . For the optical contrast measurements, the spectra were taken after 60 s of polarization. For write–erase efficiency, double step potentials of -0.5 V and +0.6 V were applied

with a rate of 1.5 V/min. The injected charge was obtained by integration of the current over the time of polarization. For response time measurements, the spectra were taken at each 5 cycles at different scan rates.



**Figure 5**. Optical contrast of PANI thin film grown at (a) **Table 3.** Electrochromic properties.

	% $\Delta T$ at 650nm	$\%\Delta T_{max}$	Colored
		/wavelength (nm)	efficiency
			$(C^{-1} cm^2)$
P1	11.1	11.4 /686	11.4
P2	25.3	26.9 / 696	14.4
P3	20.8	22.2 /692	21.4
P4	19.3	20.3/673	13.2
P5	25.4	26 / 657	10.1

## Conclusions

Potentiostatic deposition technique is a convenient way of producing electrochromic PANI electrodes with a quality comparable to that reported in the literature [2].

## **Further investigation**

The work here presented will be continued by performing kinetic studies, building hybrid electrochromic device, e.g. PANI-WO3 and doping PANI films.

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# EFFECT OF CONCENTRATION AND TYPE OF SURFACTANT ON THE SIZE OF PARTICLE AND ON THE CONDUCTIVE PROPERTIES OF POLYANILINE

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## Abstract

The effect of type and concentration of surfactant, on the size and on the conductivity properties of PANI particles was studied in this work. The particles were obtained by microemulsion and characterized by Scanning Electron Microscopy (SEM), Thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR) and conductivity tests. PANI particles with sizes from 98 to 187 nm and from 50 to 120 nm were obtained using DBSA and DTAB as surfactant, respectively. Conductivities of 0.02 S/m for the PANI obtained with DBSA, and of 0.0369 S/m for the PANI obtained with DTAB were registered. The TGA thermograms of PANI particles showed maximal degradation between the 300 and 350 °C which corresponds to a structural decomposition of PANI. The FTIR spectrum of PANI nanoparticles shows the characteristic peak of PANI at 3420 cm-1 that corresponds to the vibrations of stretching of N-H bonds of amines.

## Introduction

The conductive polymeric nanomaterials preparation has become an important branch of research. These materials exhibit unusual physical and chemical properties and they have applications in the biomedical field, microelectronics and industrial areas [1,2]. Among the intrinsically conductive polymers, polyaniline (PANI) has attracted considerable attention due to its electrical and optical properties, as well as its easy preparation, environmental stability as conductive polymer and low price. Today, PANI is studied to be implemented in bioengineering as glucose biosensor [3,4], in medical science as degradable support for nervous tissue [5], in engineering as anticorrosion coating [6,7], in electronics as electromagnetic waves insulating [8], also in energy storage, catalysts, etc.[9,10]. In particular, the use of PANI nanoparticles enhances optical and conductive properties, which improve as the size of particle decrease. With a smaller size the doping is more effective, consolidating the chain interactions, which enhance the crystallization and the electron mobility, and improve the conductivity of PANI [11, 12].

Recently, several researchers have synthesized polymeric nanoparticles using microemulsion polymerization [13,14]. This method uses nanosized micelles as nanoreactors, which are formed from the arrangement of surfactant molecules present in a liquid. Due to the morphology of the resulting polymeric nanoparticles depends on the structure of the micelles generated by the assembly of the surfactant; structures can be spherical, cylindrical or layered [15].

In this work, the effect of concentration and type of surfactant on the size of particle and on the conductive properties of polyaniline particles was studied.

## Experimental

Dodecyltrimethylammonium bromide (DTAB) and dodecylbenzenesulphonic acid (DBSA) were used as surfactants. Ammonium persulphate was used as initiator. All the reactives were reagent grade from Sigma-Aldrich.

The surfactant (DTAB or DBSA) was dissolved in deionized water at a temperature of 3 °C, the aniline monomer was added dropwise and was stirred for 30 minutes. A solution of potassium persulphate in 1.5 M HCl was added and the mixture was stirred for 3 hours. Stirring was stopped and after 24 hours the polymer was precipitated with acetone or methanol, it was filtered and the precipitate was dried until obtain constant weight. The surfactant concentration was varied to obtain different particle sizes.

## **PANI** particles characterization

The PANI nanoparticles were characterized with scanning electron microscopy in an electron microscope Jeol model JSM 6360 LV. The samples were coated with gold to improve the constrast. The thermogravimetric analysis was carried out in a thermogravimetric balance model TGA-7 from Perkin Elmer. The IR spectra were obtained on a Fourier transform infrared Nicolet model Protege with transmittance mode in a KBr pellet. The particles were synthesized in pill form and its electrical conductivity was determined using a Fluke model 1550B Electrometer.

## **Results and Discussion**

## Morphology and particle size.

Figures 1 and 2 show micrographs of PANI particles obtained with SEM using different surfactant concentration and type. It can be observe that in both types of surfactant a concentration increase results in a decrease in particle size of PANI. Particle sizes of 98 nm and 41 nm were obtained for the highest concentrations of DBSA and DTAB, respectively. This behavior is due to the higher amount of micelles with the increasing of surfactant concentration and there are more places for starting the polymerization [15]. The average particle diameter was smaller when DTAB was used as surfactant, this is because the DTAB chains are shorter than the DSBA ones, which diminish the size of micelles, and then a minor size of particle was obtained.



Figure 1. SEM micrographs of PANI particles obtained with different concentrations of surfactant (DBSA).



Figure 2. SEM micrographs of PANI particles obtained with different concentrations of surfactant (DTAB).

Thermogravimetric degradation (TGA).

Figure 3 shows the TGA thermograms of PANI particles. In general, the samples show three weight losses. The first with 4% of weight loss, located before 100 °C is due to loss of water or other volatile components in the sample. The second, between 290 °C and 360 °C is due to degradation of the surfactants and the process of oxidation of the structure of polyaniline. The third drop between 420 and 500 °C to samples obtained with DBSA (15% of lost weight) and between 400 and 470 °C in the sample obtained with DTAB (20% of lost weight), is attributed to the thermal degradation of polyaniline [16].



Figure 3. TGA and DTGA thermograms of PANI particles obtained by microemulsion polymerization with DBSA and DTAB.

FTIR Spectroscopy.

Figure 4 shows the FTIR spectra of PANI nanoparticles obtained with DBSA and DTAB as surfactants. It was observed that the spectra are very similar to each other, appreciating the characteristic peaks of PANI at 3420 cm-1 which correspond to the stretching vibrations of NH bonds of amines; the bands at 1570 cm-1 and 1125 cm-1 which are attributed to the stretching

vibrations of C=C quinoid ring, and the band at 1490 cm-1 due to stretching vibrations of C=C in the benzene ring. The peak at 1300 cm-1 is attributed to the CN stretching vibrations, and finally, the band at 805 cm-1 may be due to vibrations of the CH out of plane on p-disubstituted rings. In the spectrum of PANI with DBSA, the peaks at 1033, 2924 and 1004 cm-1 are believed to be caused by stretching of S=O, the bond C-H in the radical CH2 and the stretching of the >CH on the benzene ring in the DBSA molecule, respectively. These peaks are associated with the presence of DBSA [17], so the data correspond to the DBSA-PANI complex. The doping reaction is shown in Figure 5 and occurs preferentially on the protonated imine sites of polyaniline [18].



Figure 4. FTIR spectra of PANI particles obtained with DBSA and DTAB.



Figure 5. PANI doping mechanism with DBSA [19].

Electrical conductivity.

The change in the conductivity of PANI nanoparticles it was to related to their size, the smaller particles obtained with the higher surfactant concentration (Figures 1 and 2) have the higher conductivity as can be seen in Table 1. This behavior can be attributed to the best packing of particles with less space between them, when the particles are smaller which improve the conductivity.

Concentration of	Conductivity	Concentration of	Conductivity
DBSA	(S/m)	DTAB	(S/m)
0.09M	1.325 X 10-3	0.5M	1.19 x 10-2
0.12M	2.001 X 10-2	1M	3.69 X10-2
0.15M	1.2269 X 10-1	1.5M	1.52 X 10-1

Table 1. Electrical conductiv	vity of PANI partic	les with DBSA and DTAB
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## Conclusions

PANI nanoparticles were obtained using DTAB and DBSA as surfactants. The size of nanoparticles diminishes when the concentration of surfactant increase and the smaller particles was obtained with DTAB as surfactant. The PANI polymerization was confirmed by FTIR and TGA analysis. The smaller particles show the higher conductivity due the best packing.

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# EFFECT OF MICROSTRUCTURE ON THE ELECTROCHEMICAL PROPERTIES OF PTMA

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Design and construction of lithium-ion batteries, as operative rechargeable batteries is an active field of study and development of materials for performance-improvement is a key issue during active research. Poly(4-methacryloyloxy-2,2,6,6-tetramethylpiperidin-N-oxyl) (PTMA) is a nitroxide-containing polymer used as an anode in organic radical batteries (ORB) - secondary lithium-ion batteries - where the reversible nitroxide/oxoammonium cation redox couple is useful for obtaining large number of battery charge/discharge cycles. In this study, PTMA was synthesize by Group Transfer Polymerization reactions and the amount of radical species present in the polymer (100%) was higher than that presented on PTMA synthesized by radical polymerization. DSC analysis of synthesized PTMA showed that the glass transition temperature (Tg) of the polymer structure occurs at 155°C -corroborated by dynamic mechanical analysis (DMA)-, which is higher when compared with Tg data for PTMA synthesized by radical methods. Electrochemical and spectroelectrochemical-Electron Spin Resonance studies evidenced the presence of two different groups of nitroxide radicals oxidized at different potential values. The difference in potential values (1.25 V) for the oxidation of both species was related to both the inductive effect of the positively-charged polymeric species generated during the first oxidation process and the reorganization energy of the entire chain. The relative amounts of the each type of nitroxide species were associated to the microstructure in the polymer, suggesting a 4:1 ratio in isotactic and syndiotactic: atactic triads, as validated by determining the tacticity by NMR measurements at 160°C, in a mixture of DMSO and o-dichlorebenzene.

# PHYSICOCHEMICAL STUDY OF COPOLYMERS BY SEC-MALS

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## Abstract

Size-exclusion chromatography (SEC) combined with on-line multi-angle light scattering (MALS) and refractometric (RI) detection has been employed for the molar mass and macromolecular parameters characterization in solution of copolymers of sodium *o*-methacryloylaminophenylarsonate (o-MAPHA-Na) with sodium methacrylate (MA-Na) and acrylamide (AAD) as function of the pH. Copolymers were prepared by free radical polymerization in aqueous media at 70 °C using potasium persulfate ( $K_2S_2O_8$ ) as thermal initiator.

## Introduction

Polymers with charges along the polymer backbone (polyelectrolytes) in solution can expand or contract as the pH or the ionic strength changes due to changes in the number of charged sites or changes in the concentration of the counter iones. From the SEC-MALS, the molar mass, radius and conformation of the polyelectrolytes can be inferred. The use of multi-angle light scattering (MALS) with a size-exclusion chromatography is extremely important for the accurate characterization of macromolecules. Since MALS is an absolute technique the molar mass are determined independent of retention time [1, 2]. Thus, shift in retention times due to the expansion or contraction of polymers such as polyelectrolytes will not affect the molar masses determined by SEC-MALS. Also, by this technique can be inferred the radius and the conformation of the macromolecule [3]. Recently, it was reported the synthesis of water-soluble copolymer from sodium *o*-methacryloylaminophenylarsonate [4] and now in the present communication we report the physicochemical study by SEC-MALS of such copolymer. The differential refractive index increment (dn/dc), molecular weight off and in-line, molecular weight distributions (MWD), polidisperdity index and conformational shape were determined. Also, the effect of pH in such macromolecular parameters of water-soluble copolymers was studied.

## Experimental

## Materials

Sodium phosphate dibasic 0.5 M in water (Fluka) and sodium phosphate monobasic 5M (Bioultra-Sigma) solutions were used to adjust the pH of the copolymers solutions. The synthesis of copolymers was reported previously [4].

## Characterization

Absolute molecular weights ( $M_w$ ) were measured in batch with a multi-angle light scattering 8angle DAWN HELEOS Wyatt detector (Wyatt Technology) operating at 658 nm wavelength, calibration constant of 1.3918e-4 1/(V·cm). The differential refractive index increments (dn/dc) were determined using a refractive index detector (Optilab rEX, Wyatt Technology) at 690 nm. For SEC MALS the system consisted of a combination of two size-exclusion chromatography columns, Waters 250 and 1000 Ultrahydrogel, 300 mm x 7.5 mm. Further, the instrumental set up contained an in-line degasser (AL Waters), LC pump (515 HPLC pump) and an autosampler equipped with a 50- $\mu$ L. All measurements (batch and continuous) were conducted at 25 °C in 0.5 M NaCl aqueous solutions at pH 4.5 and 7.0 at 0.5 mL/min of flow rate. In SEC-MALS experiments the collection interval was of 0.25 s. The software used was ASTRA 5.3.4.16 (Wyatt Technology), for data acquisition and evaluation.

## **Results and Discussion**

Figure 1 shows a typical Zimm plot corresponding to poly(*o*-MAPHA-Na) in 0.5 M of NaCl in water at pH 7, also the dn/dc plot is shown in Figure 1, dn/dc value is very important to estimate the molecular weight of polymers. In this case, both plots show an adequate fit between experimental and regression data.



Figure 1. Typical Zimm (left) and dn/dc plot (right) for the poly(o-MAPHA-Na) recorded in NaCl solution 0.5M at pH = 7

In the Table 1 are summarized the physicochemical parameters such as: molecular weight, radius and second viral coefficient in batch mode for the poly(*o*-MAPHA-Na) homopolymer and their corresponding copolymers with of acrylamide (AAD) and sodium methacrylate (AM-Na) recorded at pH of 7 and 4.5. It is evident that such parameters are affected by the composition and pH. For example, the presence of ADD or AM-Na reduces the molecular weight and radius of the copolymers in comparison with the poly(*o*-MAPHA-Na), which could be explained in terms of the reactivity of radicals and comonomers structures [4]. The electrostatic repulsion in the AM-Na could be also responsible of the noticeable change in the molecular weight of the corresponding copolymer as function of pH. Such behavior is a result of the conformational assembly of the molecules in the solvent. In this sense, the A2 is a quantification of the polymer-solvent interaction. Here A2 is always positive values and are close to zero, meaning that the strength of the interaction between the macromolecules and the solvent is equivalent to the

macromolecule-macromolecule interaction strength. Under these conditions, the solvent is a theta solvent and the chains of the copolymers (polyelectrolytes) approach an ideal configuration [5]. dn/dc values for each copolymer is also reported, such values are very important in order to determinate the absolute molecular weight [6].

Table 1 Macromolecular data for <i>o</i> -MAPHA copolymers						
polymer	Initial molar ratio	рН	dn/dc (mL/g)	Mw (g/mol)	rms radius (nm)	A2 mL/g2
Poly(o-MAPHA-Na)	_	7	0.1690	1.26E+06	70.3	1.39E-04
	-	4.5	0.1531	1.15E+06	69.0	1.38E-04
Poly(o-MAPHA-co-Na-	50/50	7	0.1776	2.26E+05	41.6	9.97E-05
AAD)		4.5	0.1684	2.79E+05	34.3	3.36E-04
Poly(o-MAPHA-Na-co-	50/50	7	0.1541	4.80E+05	40.3	2.29E-05
AM-Na)		4.5	0.1491	3.19E+05	32.3	2.23E-04
Polv(o-MAPHA-Na-co-	25/75	7	0.1463	2.91E+05	30.0	4.57E-04
AM-Na)	25/15	4.5	0.1461	1.15E+05	27.2	7.84E-04

Figure 2 shows the SEC traces corresponding to poly(o-MAPHA-Na) and their copolymers with AM-Na, The weight average molecular weight (Mw) of 1 301 000 g mol<sup>-1</sup> for poly(o-MAPHA-Na) is in agreement with the value estimated in batch measurements, see Table 1. As can it be seemed the molecular weight distribution (MWD) of the homopolymer is broad with a polydispersity index ( $D = M_w/M_n$ ) around 3. In fact, the MWD shows a bimodal distribution which is due to the combination and disproportionation termination. For the case of the copolymers, the presence of comonomer reduces  $M_w$  values and the shape of the MWD which is monodisperse and slightly narrow ( $D \sim 2$ ) in comparison with the homopolymer.  $M_w$  values of 425 000 and 247 000 for poly(o-MAPHA-Na-co-AM-Na) at 50:50 and 75:25 feed molar ratio, respectively, fit adequately with off-line measurements



Figure 2. MWDs of o-MAPHA copolymers at pH = 7

## Conclusions

SEC combined with on-line MALS and RI detection was used to estimate the molar mass and macromolecular parameters in solution of copolymers of sodium *o*-methacryloylaminophenylarsonate (o-MAPHA-Na) with sodium methacrylate (MA-Na) and acrylamide (AAD) as function of pH. Macromolecular parameters are affected by the composition of the copolymer and the pH of the solution.  $M_w$  values on-line fitted adequately with the off-line values. Finally, it was found that the MWD homopolymer is broad and bimodal in comparison with poly(o-MAPHA-Na-co-AM-Na) at 50:50 and 75:25 feed molar ratio.

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# BIOPOLYMERS AS ELECTROLITIC SUPPORTS FOR LITHIUM BATTERIES

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## Abstract

During the search for environmentally friendly and cheaper polymeric materials used as electrolytic supports the biopolymers have been considered. Chitosan is one of the most promising polymers because of its non-toxic, polycationic, biocompatible and biodegradable characteristics. The conductivity of chitosan dissolved in CH<sub>3</sub>COOH is very low  $(2.14 \times 10^{-7} \text{ Scm-1})$ . However, it can be increased to  $1.03 \times 10^{-5} \text{ Scm-1}$  when ethylene carbonate is incorporated as plasticizer. Amine group in the repetitive unit may suffer a variety of reactions and allows introducing sulfobetainic groups that can easily interact with Li+ ions. In this work, the functionalization of chitosan with propanesultone, the formation of complexes with LiClO<sub>4</sub> and LiPF<sub>6</sub>, the physicochemical characterization (IR, NMR, DSC, TGA and EIS) and its possible application in a lithium battery are presented.

## Introduction

Nowadays, the interest in the production and use of new materials from renewable source is growning. Natural polymers have excellent characteristics, Duch as biocompatibility, biodegradability, nontoxicity, and adsorption properties. Chitosan, a poly(]1,4-D-glucosamine), is a basic polysaccharide obtained by partial or full alkaline N-deacetylation of chitin. It is also a multifunctional polymer that has three types of reactive functional groups: an amino group at the C2 position and primary and secondary hydroxyl groups at the C3 and C6 positions, respectively. Chitosan and its derivatives have recently been increasing attention. Recently, research has been conducted in the application of chitosan and its derivatives to treat water and wastewater, by using them, for example, as coagulants [1], to extract heavy metal ions from aqueous solutions, [2,3] biomaterials and membrana materials.[4] Chemical modification of chitosan to generate new materials is a particular interest because such a procedure does not alter the fundamental skeleton of chitosan and enables a water-soluble polymer to be formed [5] depending on the characteristics of the group introduced.In this work, the functionalization of chitosan with propanesultone, the formation of complexes with LiClO4 and LiPF6, the physicochemical characterization (IR, NMR, DSC, TGA and EIS) and its possible application in a lithium battery are presented.

## Experimental

## Synthesis of N-propilsulfonic acid chitosan (CPA)

The chitosan used was redeacetylated by a aqueous disolution of NaOH at 40% w/w, using 26 mL of this solution per gram of chitosan. The mixture was heated up to 70  $^{\circ}$  C overnight according to [6]. The chitosan was recovered by filtration and washed until the residual water had a pH of seven, and then washed with acetone and dried to vacuum to 50 °C. The deacetylation degree was of 98%, determinate by elemental analysis and conductimetric titration [2].

The chitosan deacetylated was reacted with 1,3-propanesultone according to [3]. Aqueous solution was prepared at 2% w/w of acetic acid, which chitosan was added to form a mix of 1% w/w respect the solution, then it was heated to  $70^{\circ}$ C with stirring until all chitosan was dissolved. 1,3-

propanesultone was added in a ratio of 1 mol of chitosan to 1.5 mol of 1,3-propanesultone, it was allowed to react overnight. The product was precipitated and rising the pH about of 12, filtered and washing with distillated water until that pH of residual until water was 7. The product looks like a gel slurry, it was washed with acetone and drayed to vacuum to 50°C. The degree of functionalization was determined by Elemental Analysis and was of 97%. In Figure 1 is shown the reaction of functionalitation.



Figure 1. Schematic reaction of functionalization of chitosan (CPA)

The N,N-dimethyl, N-propylsulfobetaine chitosan (CSB) was prepared by methylation of Npropylsulfonic acid chitosan with iodomethane according to [4,5] In Figure 2 is shown the reaction of quaternization.3g of chitosan and 7.3g de NaI was mixed with 100 mL of 1-methyl-2pyrrolidone (NMP). It was heated to 60°C, the mixture was stirred until that was dissolved, then 16.5 ml of NaOH was added. After the mixture was homogenized and the temperature was restored, 17.25 mL of iodomethane was added; the mixture was allowed to react overnight. The product was precipitated with ethanol and filtrated, washed with acetone and dried in oven to vacuum and 50°C overnight. The product was characterized by FTIR, 1HNMR, DSC and TGA.



Figure 2. Quaternized chitosan reaction (CSB)

#### .Polymer-salt systems

1:1 mol of polymer and salt (LiCl0<sub>4</sub> and LiPF<sub>6</sub>) were dissolved in trifluoroethanol-H<sub>2</sub>O. The solution was continuously stirred for 24 h at room temperature or until the solution looked homogeneous and then dropped into a circular Teflon mold. Residual solvent was slowly evaporated. The samples ware kept in a desiccator until their further use. These systems were labeled CPQ/LiClO<sub>4</sub>, and CPQ/LiPF<sub>6</sub>.

## **Polymers Characterization**

Elemental analysis was used to verify the chemical functionalized of the polymers. FTIR spectra were collected on a 1500 Perkin Elmer apparatus with a 2cm-1 resolution, and samples were measured in the form of dispersion in KBr dried discs. Thermogravimetric measurements were

performed with a PIRYS Perkin Elmer under a 50 cm3/min nitrogen flow. Differential scanning calorimetry was carried out under a nitrogen flow (50 cm3/min) with a MDSC2920 Modulated Differential Scanning Calorimeter manufactured by TA Instruments (Newcastle, Delaware, USA). Modulated DSC scans were carried out at 5 °C/min with amplitude of  $\pm$  0.5°C and a period of 40 seconds within the range of -50 to 180°C at a heating rate of 10 °C/min under 50 ml/min of nitrogen within the range of 30 to 500°C. The Tg reported of sample was obtained of the 2nd or 3rd scan, previous heating at 100°C and further isothermic process at 100 °C for 180 min to eliminate the maximum water absorbed on the sample.

## **Impedance Measurements**

After the synthesis, the samples were put in a desiccator until the electrochemical measurements were carried out. This was done in order to prevent the humidity of air, since residual water in the electrolytes would greatly affect the ionic conductivity of the electrolytes. For the impedance measurements, the samples (0.7 cm in diameter and 0.08 cm thick) were sandwiched between stainless steel electrodes using a two-electrode configuration. The samples were dried overnight in a Dry box, under Argon atmosphere and silica gel as desiccant agent. Temperature was controlled in the cell and the range covered was from 298 K to 343 K. A Potentiostat/Galvanostat VMP3 – Multi from Biologic Science Instruments, was used to apply potentials and to measure the impedance response in the frequency range of 1 MHz - 0.1Hz.

## **Results and Discussion**

Table I shows the analyzed carbon(C), hydrogen(H), nitrogen(N), and hydrogen (H) contents in chitosan and all modified polymers, and elucidates the relationship between the weight ratio of carbon over nitrogen (C/N) and degree of sulfonation. The C/N and the degree of sulfonation (C/N) were also strengthened and the experimental degree of sulfonation agreed relatively well with the theoretical value.

Sample	%C	%H	%Nexp	%C/%N	%C/%N	% chemical
	exp	exp		theorical	experimental	modification
Chitosan (C)	39.49	7.49	67.15	5.20	5.52	80.5
Chitosan				5.20	5.14	98.5%
deacetylated (CD)						
Chitosan N-	36.9	6.15	4.71	7.71	7.83	97.0
propilsulfonic						
acid (CPA)						

Table I. Degree of fuctionalitation of chitosan fron Elemental Analysis

FTIR spectra of chitosan raw and chitosan that is derived from 1,3-propane sultone were obtained. The FTIR spectrum includes the stretching vibration of OH group in sulfonic acid at 2900, characteristic absorption bands of the group at 1200–1000 cm\_1, stretching vibration of sulfoxide in sulfonic acid at both 1165–1150 cm<sup>-1</sup> and 1350–1340.20,21 revealing the presence of sulfonic groups in the modified chitosan. The typical bands from -SO3H group might find around of 1040 cm-1 and 1195 cm<sup>-1</sup> for symmetrical and asymmetrical stretch but is hard to see them because in the same region is found the ether, R–OR, and C-OH vibrations . However, it is clear the band of 2922 cm<sup>-1</sup> assigned to the CH<sub>2</sub> vibration of propyl group.

On the other hand, the solubility of sulfonated chitosan revealed that it was soluble not only in 2 wt % aqueous acetic acid solution but also in distillated water, and insoluble in any organic solvent, suggesting that the preparation of sulfonated chitosan via a sulfonation reaction was complete to improve the water absorption without losing the organic solvent resistance due to the

increase of its polar character.

Figure 3 shows TGA thermograms of CPA and chitosan raw. The sulfonated chitosan undergoes a three-stage decomposition. The first stage is between 50 °C and 120 °C with a loss of almost 8% of the initial weight. It is followed by a further 40% weight loss just above 200°C, ending at approximately 290°C, which involves the decomposition of the pendant sulfonate groups of the chitosan polymer. The third stage of decomposition, which ends at around 400°C, involves a weight loss of around 15%. The thermal stability of CPA decrease from 317 °C to 246 °C when it is compared with chitosan raw, at the same decomposition temperature (Td) of 10% of weight loss. This decreased of CPA in its thermal stability is due to reduction of its capability to form a hydrogen bond by introducing the propylsulfonic acid group. This change might render the material more hydrophilic and destroy the crystalline structure. Eventually after sulfonation, the structure of the polymer became irregular, deteriorating the thermal properties.

No Tgs are seen for any sample of chitosan and N-propanesultone chitosan by DSC thermograms (figure not include here).



Figure 3. TGA thermograms for Chitosan raw and CPA

The deacetylation of used chitosan was confirmed by 1HNMR, the figure 4 show the spectrums, the figure 4(a) show the spectrum for chitosan commercial partially deacetyled, chemical shif in 2.1 ppm for methyl of ammine; in the figure 5(b) the chemical shift was demised.



Figure 4. 1HNMR spectrum for commercial and re-deacetyled chitosan.

The deacetyled chitosan was reacted with 1,3-propanesultone to form the N-propanesultone chitosan, the signals of the proton of methylene is observed in 2.2 and 3.1 ppm of chemical shift correspondint to propanesultone. Figure 6 show the spectrum; CD spectrum corresponding to chitosan and CPSAA to sultonated chitosan.

Efforts to measured ionic conductivity and its posible use in a lithium battery are currently underway.



Figure 6. 1H-NMR of CD and CPSAA

## Conclusions

Chitosan is a highly reactive polymer with its active side chain amino group. This characteristic is taken advantage in modifying the chitosan using 1,3-propane sultone to produce water-soluble chitosan with different numbers of amino groups. EA, FTIR, and <sup>1</sup>H NMR demonstrate that the sulfonation was successful. The solubility and the chemical resistance increased over a wide range of pH values of sulfonated chitosan, suggesting that modification strengthens the interaction between water and the chitosan chains. This results show that chitosan functionalized could be used as solid electrolyte and separator in a lithium battery.

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# DEVELOPMENT OF P. PUTIDA BIOFILMS ONTO POSTCONSUMER AGAVE FIBER/LDPE COMPOSITES

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## Abstract

An eco-friendly support for bacterial immobilization was produced by extrusion. The support is a composite material made of recycled polyethylene and chemically treated or non-treated fibers of *Agave Tequilana* Weber var. Azul. The fibers were previously cleaned and some of them were treated with NaOH in order to eliminate lignin. The composites were obtained by extrusion with a screw speed of 30 rpm using a rectangular die to obtain 2 cm wide ribbons. Biofilms were developed in batch experiments using glucose or benzene as carbon source. FTIR-ATR and SEM analyses showed that *P. putida* F1 were adhered onto both composite surfaces and their ability to develop a biofilm using both carbon sources. An image analysis of the SEM micrographs was carried out to quantify the biofilm development, showing that the process is more efficient when composites with treated fibers were used.

#### Introduction

The use of immobilized cells or microorganism in reactors offers many advantages over suspended cell systems like: easier separation, greater operational flexibility and higher cell density resulting in higher rates of biodegradation per reactor unit volume [1]. It has also been reported that immobilized cells are protected from harsh environmental conditions becoming more tolerant to high concentrations of toxic compounds [2]. In this sense, there is a continuous search for more efficient, easier to handle and low-cost supports.

The immobilization of cells can be done by different available methods: covalent coupling, crosslinking, physical entrapment and the natural process of adhesion. The natural adhesion method has as main advantages the maximum cell viability and the biochemical activity due to the biofilm formation after adhesion [3].

On the other hand, recycling of polymers is a very important environmental aspect. Recently, one alternative that has taken a relevant importance is the production of natural fiber-polymer materials whose main application is the production of construction materials. In addition, the fiber wasted throughout the process of Tequila production is a specific pollution problem taking place in South-west Mexico. There are some works reporting the use of agave fibers mixed with thermoplastics for the production of composites [4].

In this sense the objective of this work is the production of an eco-friendly support for bacterial immobilization. The support is a composite material made of recycled polyethylene and treated or non-treated fibers of *Agave Tequilana* Weber var. Azul. The study provides information for the potential use of composites as carriers for microorganism immobilization to its application as an efficient and eco-friendly biotechnology

## Experimental

## Bacterial strain and media

The microorganism used in this research was *P. putida* F1 ATCC 700007 (AmericanType Culture Collection, Manassas, VA). The growth medium is reported in Robledo-Ortíz et al., [5]. Two carbon sources were used for biofilm development: glucose (Analytyka, Tecnología Industrial Química, México) and benzene (HPLC, Sigma, St. Louis, MO, USA).

## **Composite preparation**

The composite employed as support for the immobilized bacteria was made using recycled lowdensity polyethylene (LDPE), fibers of *Agave Tequilana* Weber var. Azul, obtained from a local tequila company, and Azodicarbonamide (ACA), as blowing agent from Sigma-Aldrich (USA). The fibers were previously cleaned and one batch of them was chemically treated (digested) with NaOH in order to eliminate lignin which produces an inhibitory effect for bacterial growth. The digestion was carried out in a lab-scale digester with a 20% (w/w) NaOH solution and a temperature of 170 °C for 90 min. After digestion, the fibers were water-washed and air dried. Afterwards, a 0.5% amount of ACA (wt/wt) and 0.1% of ZnO (wt/wt) as catalyzer were added to a blend of 30% fiber (treated or non-treated) and 70% recycled polymer and extruded in a singlescrew Haake Rheomex 254 extruder controlled by a Haake Rheocord 9000 control system. The temperature profile was set to 150/160/170/180 °C with a screw speed of 30 rpm using a rectangular die to obtain (2cm wide × 0.15 cm thickness) ribbons. After the extrusion process, the ribbons were cut to obtain rectangular pieces of an average size of  $7 \times 9 \times 1.5$  mm, which were used as bacterial support.

## FTIR-ATR analysis, SEM observations and Image analysis

For SEM observations, the composite ribbons with attached bacteria were washed three times with 10 mM NaCl solution to remove non-adhered cells. Afterwards they were observed in a scanning electron microscope Tabletop Hitachi TM-1000. Image analysis of SEM micrographs was carried out by using MATLAB software. Additionally, the sample ribbons were directly analyzed in a Perkin-Elmer Spectrum 100 FTIR spectrometer with a Universal ATR accessory to observe peaks related to proteins, exopolysaccharides, water, and lipids due to biofilm formation.

## **Results and Discussions**

Figure 1 shows a comparison of the composite surface covered by biofilm with glucose as carbon source at concentrations of 0.1 and 1% (wt/wt) respectively. There can be appreciated the dependence of the biofilm development with the time and the substrate concentration. While in the graph with glucose at 0.1% is observed a period of 12 days to achieve a geographic distribution of almost 100% in samples with 1% only 8 days to reach this percentage were needed.

The effect in the biofilm development of using treated and untreated fiber in the composite conformation becomes important at the beginning of the immobilization procedure, nevertheless at the end of the growth process in both cases the same results were achieved in the area covered by the bacteria after the same time. This initial disadvantage is due to the presence of lignin in the untreated fiber composites, although the subsequent recovery in the biomass growth rate suggests an adaptation of the bacteria to lignin, after which the biofilm continues to grow at a higher rate to achieve the same overall rate as the biofilm in the composites with treated fiber.



Figure 1. Surface covered by biomass using 0.1% (left) and 1% (right) of glucose as carbon source.

Figure 2 shows the progress in the area covered by biomass in a period of 8 days for composites with treated and untreated fiber using benzene as carbon source. As expected, the biofilm growth is function of the concentration of aromatic compound. It is also clear that the bacterium does not grow as easily in a medium with benzene as it does in a medium with glucose. This could be due to the lag phase which is the period needed for the bacteria to be adapted into the new medium or carbon source. The adaptation period is related to the activation mechanism of the enzyme toluene-dioxygenase (TDO) which is necessary for the degradation of the aromatic compound.

Once again, the effect of the presence of treated or non-treated fibers is presented, nevertheless, at high concentrations of aromatic compound it seems to be more important. The production of catechol which has been reported as an inhibitor of the degradation process [6] in addition to the inhibitory effect to bacterial growth produced by the lignin presented in non-treated fibers [7], could explain the behavior observed in Figure 2 for 60ppm of benzene.



peak at  $3400 \text{cm}^{-1}$  is typical of hydroxyl groups (-OH) found in the cellulose and, as expected, there is observed with a greater intensity in the composites with treated fiber. The same result can be observed with the peaks located in the range of 900-1200 cm<sup>-1</sup> which are associated with the glucopyranose ring structure (the repeat unit of cellulose). Other signs associated with the group -CH<sub>2</sub>- corresponding to polyethylene can be observed at 2912 and 2848 cm<sup>-1</sup>, besides the peak at 1460 cm<sup>-1</sup>, related to the long chains of the polymer. The signal at 1734 cm<sup>-1</sup> corresponds to the carbonyl groups -C=O of lignin and it is possibly to observe a considerable decrease in its intensity for treated fiber composites compared to untreated fiber. This verifies the correct application of the process of fiber digestion [8].



Figure 3. FTIR-ATR spectra of composites with non-treated fiber (left) and treated fiber (right).

Figures 4 shows the FTIR-ATR spectra for the cases of biofilm growth with benzene and glucose as carbon source on treated fiber composite. After day zero, the spectrum begins to reflect the presence of macromolecules that constitute the biofilm such as polysaccharides, proteins, lipids and water. The signals due to amide I and amide II groups (1540 - 1650 cm<sup>-1</sup>) which are associated with proteins and the water related peak whose signal is due to hydroxyl groups (3200-3600 cm<sup>-1</sup>) clearly increased during biofilm growth, as can be observed in the spectra corresponding to the 3, 5 and 7 days in the case of benzene and 6, 10 and 12 days in the case of glucose.



Figure 4. FTIR-ATR spectra of composite surface covered by biomass using 30ppm of benzene (left) and 0.1% of glucose (right) as carbon source.

On the other hand, the signals of polysaccharides (900 - 1200 cm<sup>-1</sup>) and lipids (2850 to 2970 cm<sup>-1</sup>)

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are not clear due to the interference generated by the typical signs of polyethylene and cellulose agave fiber material present in the compound. Hadjiev et al., [8] used the FTIR-ATR technique to analyze the formation of biofilms on various polymeric substrates with similar results. Both spectra are from treated fiber samples to show more clearly the peaks corresponding to proteins without the interference caused by the group of lignin (to 1734 cm<sup>-1</sup>) present in the untreated fiber materials.

#### Conclusions

*P. putida* F1 biofilms were developed successfully onto composites of LDPE and treated and untreated agave fibers as shown in SEM micrographs and FTIR-ATR spectra. It was observed that the initial rate of biofilm growth is higher in the material with treated fibers, nevertheless at longer times both materials are covered 100% by microorganisms. The previous results were observed in both carbon sources used, benzene and glucose.

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# **REGENERATION OF CHROMIUM (VI) COMPOSITE SORBENTS MADE OF POLIETHYLENE AND AGAVE FIBERS COATED WITH CHITOSAN**

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## Abstract

A composite of high density polyethylene and agave fibers (*Tequilana* Weber var. Azul) coated with chitosan was prepared; afterwards the composite was used for the adsorption of chromium (VI) showing a maximum adsorption capacity of 200 mg / g chitosan. The main objective of this study was to find the best desorbent for chromium (VI) in order to reuse the material. In this sense, solutions of sodium hydroxide and sulfuric, nitric and hydrochloric acids were used in desorption experiments at concentrations of 0.1 and 0.5 M [1]. SEM micrographs were taken of composite samples before and after desorption processes and analyzed by FTIR-ATR spectroscopy.

The results showed that a better desorption is obtained using 0.1 M concentrations. The best chromium desorption was achieved with sulfuric acid. Nitric and hydrochloric acids deteriorate the material causing chitosan detachment. Sodium hydroxide causes deprotonation of the amine groups of chitosan, which are primarily responsible for adsorption [2].

## Introduction

Composites made from natural fibers and thermoplastic materials (NFC) bring to material engineering new options and solutions in product development [3]. Chitosan is a natural macromolecule widely studied as heavy metal sorbent; it interacts with metal ions to form a chelate [4]. Nevertheless chitosan handling is complicated since it tends to swell and finally to solubilize in slightly acidic solutions. In this sense, is essential to obtain a suitable, manageable and cost-effective material to be used as support for the chitosan in order to use it in processes for removal of heavy metals from contaminated water. Using a support material such as NFC is an alternative to the disadvantages of using chitosan in its natural form and in addition, if this material has the possibility to be reused; it would be even more attractive.

## Experimentation

## Materials

The materials used in this study were HDPE (PADMEX 65050, PEMEX) and residual agavefibers from a local tequila company. Azodicarbonamide (ACA) as a chemical blowing agent, Chitosan powder with 95% deacetylation. Potassium dichromate, acetic acid and 1,5 diphenylcarbazide. Sodium hydroxide and nitric, sulfuric and hydrochloric acids from Sigma-Aldrich.

## **Composite preparation**

The composite was produced using 70% HDPE and 30% agave fiber (wt/wt); the HDPE was mixed with 1% ACA. Prior to the mixing, the agave fibers were cleaned to eliminate the solids. Afterwards, the composites were extruded in a double-screw extruder Leistritz micro 26 GL/GG-36D. After extrusion, the material was pelletized. The composite pellets were treated with a chemical process to incorporate chitosan. This treatment consisted of composite immersion in an alkali bath (10% wt NaOH) for 24 h followed by an immersion in a 2% v/v acetic acid solution.

The material was dried in a solar dryer for one day. Afterwards, 100 g of dried pellets were immersed in 500 mL of chitosan solution (2 % wt/wt) previously dissolved in 2% v/v acetic acid, and dried. Finally, the pellets coated with chitosan were washed with distilled water to remove the excess chitosan and dried before their use.

## **Adsorption-Desorption cycles**

Adsorption-Desorption experiments were conducted in batch systems using initial Cr (VI) concentrations of 300 mg/L prepared from potassium dichromate. The experiments were carried out in 15 mL glass vials by contacting 1 g of composite with 10 mL of Cr (VI) solution for 4 h (time to reach equilibrium) in a reciprocal Barnstead Shke5000-7 shaker at 25 °C and a 150 rpm. After reaching the equilibrium the sorbent was filtered from the solution and the filtrates were analyzed for Cr (VI). In order to determine the reusability of the sorbents, consecutive adsorptiondesorption cycles were repeated. Cr (VI) was desorbed with, 0.1 and 0.5 M solutions of HCl, H<sub>2</sub>SO<sub>4</sub>, NaOH and HNO<sub>3</sub>. After adsorption, the material was washed with DI water. The material loaded with chromium was placed in 10 mL of desorption medium and stirred at 150 rpm for 1 h at 25°C. This adsorption-desorption procedure was repeated six times. After desorption, the sorbent was washed with distilled water and used in the succeeding cycle. The amount of chromium desorbed was calculated from the amount of chromium adsorbed on the adsorbent and the final chromium concentration in the desorbed solution. Chromium concentration was quantified using a colorimetric method [5]. Finally SEM micrographs were taken using a Hitachi TM-1000 Tabletop Microscope in order to observe the effect of the chemical used as desorbent over the chitosan supported in the composite.

## **Results and discussion**

Adsorption-desorption cycles were conducted successfully; the material had the capability to adsorb a great amount of Cr (VI). Table 1 presents the data obtained after 6 cycles for each desorbent. The data showed that 0.1 M solutions have better performance than 0.5 M solutions. It can also be observed that the best desorbents would be hydrochloric acid, followed by nitric acid, nevertheless SEM micrographs of the material suggested that  $H_2SO_4$  is the best option as will be discussed later. Dantas et al., [1] performed desorptions of Cr (VI) with different acids and found that the best of them is sulfuric acid, reporting a 100% Cr (VI) desorption. Boddu et al., [6] performed the desorption process with 0.1 M sodium hydroxide and reported that the material is completely regenerated.

Desorbent	% Desorption	% Adsorption
$H_2SO_4 (0.1 M)$	29	71
$H_2SO_4 (0.5 M)$	10	68
HNO <sub>3</sub> (0.1 M)	29	89
HNO <sub>3</sub> (0.5 M)	6	83
HCl (0.1 M)	27	91
HCl (0.5 M)	19	88
NaOH (0.1 M)	9	21
NaOH (0.5 M)	8	18

Table 1. Percentages of Chromium (VI) adsorbed and desorbed (after six cycles).

Adsorption-desorption cycles with 0.1 M solutions are presented in Figure 1. There is a similar behavior in the cycles with nitric and hydrochloric acid as shown in Figure 1 a) and b). The material adsorbs a high percentage of chromium between each cycle despite the low desorption. Some studies reported that an amount of Cr (VI) desorbed is due to these acids dissolving the chitosan [8]. Babel and Kurniawan [9] carried out a chitosan treatment with nitric acid which significantly improved its adsorption capacity. The HNO<sub>3</sub>, causes an increased on the exposure of the amine groups and consequently increases the number of active sites, nevertheless a considerable amount of Cr (VI) to Cr (III) which also could explain the high efficiency showed in Table 1. In the case of sulfuric acid (Figure 1 c) the efficiency appears to be slightly lower than HNO<sub>3</sub> and HCl but an important fact is that chitosan is not soluble in this acid making it a good desorbent [7].



Figure 1. Adsorption-Desorption cycles in: a) sulfuric acid, b) nitric acid, c) hydrochloric acid, d) sodium hydroxide.

Desorptions with sodium hydroxide did not give good results as can be observed in Figure 1 d). The material loses its adsorption capacity after being treated with this compound. An explanation for this phenomenon is the deprotonation of chitosan amine groups at alkaline pH.

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SEM micrographs of the compound were taken in the different processes to observe changes in the material. Figure 2 a) shows the composite of polyethylene and agave fiber and Figure 2 b) shows the composite coated with chitosan. It is possible to observe the differences in the surface material due to the chitosan presence.



Figure 2. a) Composite of polyethylene and agave-fiber and b) composite with chitosan.

Figure 3 shows the composite surface after six adsorption-desorption cycles. It is possible to observe that chitosan has been extensively removed when (a)  $HNO_3$  and (b) HCl are used. On the other hand with sulfuric acid (c) the chitosan remains attached to the composite surface.



Figure 3. SEM micrographs for desorption with a)  $HNO_3$ , b) HCl, c)  $H_2SO_4$  and e) NaOH

Second US-Mexico Meeting "Advanced Polymer Science" and XXIV SPM National Congress Riviera Maya, Q. Roo, México. December 2011 Finally, for NaOH (d) even when chitosan remains onto the surface, this material is no longer suitable to be used as a Cr (VI) sorbent as shown in Figure 1 d).

## Conclusions

According to the results the four solutions used are able to desorb the chromium from the material prepared, but each has some drawbacks. Sodium hydroxide fosters deprotonation of the active sites of chitosan causing losses in adsorption capacity; nitric and hydrochloric acids lead to a good adsorption while doing damage to composite material like a decrease of its physical properties and chitosan detachment; although the material desorbed in sulfuric acid does not regenerate at 100% is the solution that provides the best performance, since the material continues desorbing and adsorbing Cr (VI) while retaining its original properties.

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# EFFECT OF NATURAL AGEING ON THE MECHANICHAL PROPERTIES OF POSTCONSUMER WOOD/POLYPROPYLENE COMPOSITES

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#### Abstract

In order to ensure better quality and higher durability of WPC's used on exterior environments is necessary to understand the effect of natural ageing on their physical and mechanical properties. In this sense, wood-polypropylene (PP) composite pellets were produced by extrusion varying the particle size (60, 100 and fines) and wood-polymer ratio (30-67, 40-57 and 50-47); 2% of coupling agent MAPP and 1% of calcium stearate (dispersing agent) were added to the blends. Afterwards, the pellets were processed by injection molding to obtain specimens for testing. The samples were evaluated at initial time and after four months of exposure to natural ageing. FTIR-ATR and SEM analyses were also carried out to observe changes in morphology and surface composition.

FTIR-ATR results showed formation of carbonyl groups due to photodegradation of wood and PP and SEM analyses revealed composite surface microcracking. In general, a decrease on impact strength and bending MOE was observed while bending MOR increases. Weathering had no significant effect on tensile MOE while tensile MOR also increased.

#### Introduction

Wood plastic composites (WPC's) had been widely used in construction, furniture and automotive industries in USA, Europe and Asia. The success of WPC's was due to good performance on exterior environments [1,2]. However, currently there is evidence that performance of WPC's is affected by natural ageing causing color changes, xylophagous fungi development and reduction of mechanical properties affecting life service of WPC's [3].

Wood species, polymer type, wood particle size, wood/plastic ratio, addition of coupling agent, exposure time and environmental conditions (humidity and radiation) are factors that affect WPC's performance on exterior environments. WPC's exposure to natural ageing could generate surface micro-failures (microcracking) due to moisture sorption by wood particles and further swelling, causing a compression effort over polymeric matrix weakening wood-polymer interface reducing mechanical properties and creating a path for moisture movement into composite matrix [4,5,6]. Solar radiation cause discoloration, severe micro-failures, accelerated damage and fungi development affecting negatively mechanical properties and exterior performance [7,8].

The objective of this research was to know the effect on accelerated ageing on mechanical properties of wood/recycled polypropylene composites. WPC's were prepared using different wood/plastic ratios, particle sizes, coupling agent (MAPP = Maleic Anhydride Polypropylene) and Calcium Stearate as dispersant.

## Experimental

## Materials

Pine sawdust, Pinus spp (*P. leiophylla*, *P. douglasiana*, *P. oocarpa*) was collected from a local sawmill. Sawdust was pre-dried (10% moisture content) and then wood particles were classified using mesh sizes 20, 40, 60, 100 and fines. Wood particles retained on mesh sizes 20 and 40 were
cut in order to generate smaller particle sizes. The classified particles were finally dried (2% moisture content) on a laboratory stove at 80°C.

Polypropylene (pp) recovered from a primary process that produces pampers donated by Camaleón Pigmentos S.A. de C. V was used as matrix (MFI = 50 g/10 min). Additionally MAPP (Maleic Anhydride Polypropylene, OVERAC CA 100, Macropol S. A.) and Calcium Stearate (TPW-104, Struktol) were used as coupling agent and dispersant respectively.

# Wood-polypropylene mixtures

Nine wood-polypropylene blends were prepared, 30-67%, 40-57% and 50-47% and three wood particle sizes, mesh sizes 60, 100 and fines. It was added to each prepared formulation 2% MAPP and 1% Calcium stearate. Finally, in order to compare WPC's properties a 100% pure polypropylene was run.

# **Extrusion and Injection**

Material blends were prepared using a double-screw extruder Leistritz micro 26 GL/GG-36D. The extruder temperature profile was set between 150 °C and 190 °C from the barrel to the die at a screw speed of 60 rpm and a feeder speed of 175 rpm. Cooling of the extrudate at the die exit was performed in water at room temperature. After extrusion, the blends were pelletized.

WPC's specimens were produced in a Nissei ES1000 injection moulding machine. The temperature profile was set to  $160/170/185/200^{\circ}$ C; injection pressure 115 MPa, retention pressure 70 MPa, injection time 14 s, retention time 6 s and cooling time 30 s. The mould temperature was maintained at 30°C, and injection speeds were V<sub>1</sub>=40, V<sub>2</sub>=15, V<sub>3</sub>=35 (mm/s).

# Natural ageing of wood-polypropylene composites.

Wood-polypropylene specimens of each formulation were exposed to natural ageing from September 2010 to January 2011at the Department of Wood Cellulose and Paper facilities, UdG., México. Exposure was characterized by periods of solar radiation, rain and wind, temperature variation from -2 °C to 38°C. 100% pure polypropylene specimens were also exposed under similar conditions.

# Morphologic characterization and infrared spectroscopy ATR-FTIR

Micrographs were obtained using a scanning electronic microscope (SEM), HITACHI TM-1000. Infrared spectrums were obtained using a Perkin Elmer Spectrum GX with an ATR accessory. Specimens used to obtain spectrums before and after natural ageing treatment were pp 100% and wood-pp, 50%, mesh size 100. Two measures were done and each spectrum obtained was the average of 16 screenings, range 4000 to 500 cm<sup>-1.</sup>

# Determination of mechanical properties.

Mechanical properties were determined before and after treatment for each wood-pp formulation and 100% pp tested. Impact strength, bending MOE and MOR and tensile were obtained according ASTM standards [9, 10, 11].

# **Results and Discussion**

# Surface morphological evaluation

In micrographs (figure 1) surface microcracking of neat pp (A) and wood-pp composite (B) can be

observed. In the first case, it could be attributed to polymer crystallinity that generates a shrink of surface layer caused by photo-oxidation [12]. In the second case, micro-failure increases due to moisture effect in wood-polymer interface. Sever surface microcracking was associated to higher content of wood and larger wood particles. It could be due to a deficient coating of the wood particles by the polymer.



**Figure 1.** Composite surface microcracks after being exposed for four months to natural ageing, (A) neat polypropylene and (B) wood particles-polypropylene (47-50), mesh 60.

# **ATR-FTIR composite surface analysis**

Figure 2 (a) shows an increase in the pick corresponding to the carbonyl groups (C=O, 1720 cm<sup>-1</sup>) after natural ageing and also an effect in the signals of aromatic groups related to the lignin (1450 y 1600 cm<sup>-1</sup>) which is the wood component with a higher photodegradation [13]. In the pp spectrum (figure 2(b)) is possible to observed after the ageing an intensification in the hydroxyl groups band (O-H, 3400 cm<sup>-1</sup>), picks corresponding to C-O bonds (1040, 1100 y 1170 cm<sup>-1</sup>) due to the formation of alcohol groups and a strong band corresponding to carbonyl groups stretching (1715 cm<sup>-1</sup>) which could be associated to carboxylic acids and ketones. The signal at 1600 cm<sup>-1</sup> is possible to observe strong bands at 1717 cm<sup>-1</sup> and 1600 cm<sup>-1</sup> related to the formation of carbonyl groups and carbons with a double bond at the alpha position respectively, probably due to lignin and pp photodegradation. An increase in the bands at 1040, 1100 y 1070 cm<sup>-1</sup> related to C-O bonds (associated to formation of alcohol groups) is presented and confirmed by the band at 3340 cm<sup>-1</sup> corresponding to hydroxyl groups.



Figure 2. ATR-FTIR spectra (a) wood particles, mesh 100, (b) pp, (c) Composite wood-pp (47-50, mesh 100) before and after natural ageing.

# Mechanical properties evaluation

In figure 3 (a) is showed a lost in impact strength in all formulations tested, including neat pp. Composites made with wood particle, mesh 60 exhibited the lowest effect on impact strength regardless more cracks were developed.



Figure 3. Effect of accelerated ageing on mechanical properties of wood-polypropylene composites

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The amount of wood particles in the composite was associated with a reduction on impact strength. It was probably due to deficient coating of the wood particles by the polymer. It generates that more wood particles were exposed in the composite surfaces generating a higher photodegradation. Despite these situations, the impact strength of the composites after being exposed to natural ageing was higher than the impact strength of neat polypropylene.

Regarding bending test, most formulations exhibited MOE lost after being exposed to natural ageing (Figure 3 (b)).Composites made with high wood content showed higher MOE lost that was strongly associated to microcracking increase. Meanwhile MOE and MOR (Figure 3 (c)) of neat pp were increased after being exposed to natural ageing. This behavior was observed in all tested specimens. According to Ragnar et al., [11] this phenomena could be attributed to a rearrangement of pp on internal layers of the composite generating a photo-oxidation of the pp that is reduced when wood content is increased. Regarding tensile strength test (Figure 3 (d)), no effect of natural ageing was observed on MOE. Neat pp specimens showed a significant increase (P < 0.05) on MOE. In the case of tensile MOR (Figure 3 (e)), a similar trend to bending test was observed.

# Conclusions

Composite surface microcracking was more evident in formulations with higher wood content and larger particle size. Both, wood particles and neat pp undergo degradation due to photo-oxidation (carbonyl groups presence) and individually contributes to the photo-degradation of the wood-pp composite.

Natural ageing causes a higher lost in impact test in those composites elaborated with higher wood content, meanwhile the mesh 60 and 100composites exhibited better values. Bending MOE and MOR after natural ageing exhibited different behavior. Higher MOE lost was observed in composites with higher wood content; with regard to MOR trend was to increase or retain initial value. There was no evidence of the effect of natural ageing on MOE and tensile strength, however, MOR increased. At higher wood content all wood particle sizes are suitable.

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# Superposition of a random longitudinal vibration pipe and pulsating flow of a yield stress liquid.

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#### Abstract

In this work, the rectilinear Poiseuille flow of a yield stress liquid flowing in a vibration pipe coupled with a pulsating-time pressure gradient is analyzed. The pipe wall performs ultrasonic vibration (longitudinal) and pulsating flow can be adequately represented by a time Fourier series. In order to find an analytical expression for the flow enhancement a quasi-static perturbation solution in terms of a small parameter is suggested. The stress tensor is separated in two contributions, the first due to the solvent and the second to the polymer contribution. The complex liquid is characterized whit the Bautista-Manero-Puig model (BMP) constitutive equation, consisting in the Upper Convected Maxwell equation coupled to a kinetic equation to account for the breakdown and reformation of the fluid structure. The viscoelastic, kinetic and structural mechanism were characterized by the association of non-dimensional numbers to each mechanism. Finally, flow enhancement is predicted using experimental data reported elsewhere for a worm-like micellar solutions of CTAT.

#### **1. INTRODUCTION**

The analysis of the oscillating pressure gradient flow of Newtonian and non-Newtonian fluids has attracted ample interest due to several applications, among them, in bio-fluid mechanics biorheology, enhanced oil recovery operations a others. In biorheology, examples are the flow of blood in veins which is forced by a periodic pressure gradient (Herrera et al., 2009, 2010) and interesting manifestations of biological fluid flow such as the flow of spider silk [1-3]. From a practical point of view, pulsatile flow of complex liquid (worm-like micellar systems and lyotropic liquid crystals) has applications in enhanced oil recovery operations. In addition, pulsating and oscillating flows are important in the industrial applications such as polymer extrusion using oscillatory dies.

Theoretical predictions using perturbation and numerical methods on viscometric flows (or nearly viscometric flows) of the flow enhancement as a function of the frequency and amplitude of oscillations have been reported (Herrera et al., 2009, 2010) using viscous and viscoelastic equations of state (Herrera et al., 2009 and 2010). In most analyses, it is shown that the shear-thinning is the principal mechanism behind flow enhancement and that this enhancement is proportional to the square of the relative amplitude of the oscillating pressure gradient and its magnitude depends on the shape of the viscosity function. Other important factors are the waveform (triangular, sinusoidal and square type) that has a strong effect on flow enhancement and power requirements (Herrera et al 2009, 2010). Notwithstanding, there is still open questions and

lack of the theoretical and experiments studies dealing with complex fluids and complex behavior such as thixotropy, rheopexy and shear-banding flow in pulsating and oscillating flows.

# 2. PROBLEM FORMULATION

The isothermal rectilinear flow of a structural complex liquid under a pulsating time pressure gradient is analyzed in a circular pipe of radius r = a and axial z = L. Entry and exit effects and gravitational forces are neglected. In this system, all physical quantities in cylindrical coordinates are defined with respect to an origin at the pipe centre. The axial fluid velocity is a function of z = L, and both the non-slip condition and symmetry of the velocity field are applied. The pulsating pressure gradient here is represented by, where n(t) is a pressure gradient noise and  $\varepsilon$  is a small parameter.

# **3. THEORETICAL EQUATIONS**

In this section it is presented the balance momentum equation and constitutive equation that describes the complex flow system

$$\varepsilon \rho \frac{D}{Dt} V = -\nabla p (1 + \varepsilon n(t)) + \nabla \cdot \sigma + \rho g$$
<sup>(1)</sup>

$$I(\%) = 100 \frac{\int_0^a \left( \left\langle \gamma(\mathbf{r}, \mathbf{t}) \right\rangle - \gamma_0^{\Box}(\mathbf{r}) \right) \mathbf{r}^2 d\mathbf{r}}{\int_0^a \gamma_0^{\Box}(\mathbf{r}) \mathbf{r}^2 d\mathbf{r}}$$
(2)

In equation (1)  $\varepsilon$  is a perturbation parameter,  $\rho$  is the density of the complex solution, p is the thermodynamic pressure, n(t) is the stochastic noise and g is the acceleration of the gravitational forces. In Equation (2), I(%) is the flow enhancement and  $\gamma^{\Box}(r,t)$  and  $\gamma^{\Box}_{0}(r)$  are the unsteady and steady shear rate respectively. Finally the symbol  $\langle \rangle$  is the average value of the unsteady shear rate.

# **3.1 CONSTITUTIVE EQUATION BMP MODEL**

$$\sigma + \frac{\eta (II_{\rm D})}{G_0} \overset{\nabla}{\sigma} = 2\eta (II_{\rm D}) D$$
(3)

$$\frac{d}{dt} Ln\eta (II_{D})^{\lambda} = 1 - \frac{\eta (II_{D})}{\eta_{0}} + k\lambda \left(1 - \frac{\eta (II_{D})}{\eta_{\infty}}\right) \sigma: D$$
(4)

Equation (1) is the modified momentum equation. It is important to note that, in equation (1), the epsilon parameter represents a small perturbation in the pressure gradient term. The second is the flow enhancement that represents the changes of the volumetric flow when a pulse is applied in a constant pressure gradient and inertial term. In equation (3)  $\sigma$  is a viscoelastic stress,  $\stackrel{\nabla}{\sigma}$  is the upper-convected derivative of the stress tensor,  $\eta$  is the viscosity function, D is the rate of deformation tensor, II<sub>D</sub> is the second invariant of D and G<sub>0</sub> is the elastic modulus. In equation

(5)  $\eta_0$ ,  $\eta_\infty$  are the viscosities at zero and very high shear rates, respectively,  $\lambda$  is the structural relaxation time and *k* can be interpreted as a kinetic constant for the structure breakdown, all five parameters of the model ( $\eta_0, \eta_\infty, G_0, \lambda, k$ ) are related to the fluid properties and can be estimated from independent rheological experiments in steady and unsteady flows.

## 4. DIMENIONLESS VARIABLES

Herrera et al. [2-3] proposed the following dimensionless variables for the axial velocity, pressure gradient, time, shear- stress, shear-rate, radial coordinate, viscosity function and frequency, respectively.

$$p = \frac{dP/dz}{\eta_0/a\lambda}; V_z^* = \frac{V_z}{\omega a}; t^* = \frac{t}{\lambda}; \tau = \frac{\sigma_{RZ}}{\eta_0/a\lambda}; r^* = \frac{R}{a}; \eta^* = \frac{\eta}{\eta_0}; \omega^* = \omega\lambda$$
(5)

Here, the characteristic time is  $\lambda$  (structural build-up time). This election of the non-dimensional variables enables the comparison with other characteristic times associated to a given physical mechanism (e.g. viscoelastic,  $\lambda_0 = \eta_0 G_0^{-1}$ ,  $\lambda_\infty = \eta_\infty G_0^{-1}$  and rupture  $\lambda_r = k\eta_0$  times).

## 5. DIMENSIONLESS NUMBERS

In order to solve the set of equation, a set of dimensionless variables are proposed, which results in a set of dimensionless groups that describe the physical mechanism in the system. Reynolds, Deborah and other dimensionless numbers are as follows:

$$\operatorname{Re}=\frac{\rho(\omega a)a}{\eta_{0}}; \operatorname{De}=\frac{\eta_{0}/G_{0}}{\lambda}; \operatorname{A}=\frac{k\eta_{0}}{\lambda}; \operatorname{B}=\frac{\eta_{0}}{\eta_{\infty}}; \operatorname{D}=\frac{\eta_{s}}{\eta_{0}}; \operatorname{C}=\left(\operatorname{AB}\right)^{1/2}=\left(\frac{k\eta_{0}}{\lambda}\frac{\eta_{0}}{\eta_{\infty}}\right)^{1/2}$$
(6)

The pulsating Reynolds number (Re) [1-3] relates the inertia and viscous forces in the fluid. The second group is the Deborah number (De), which represents the relation between two characteristic times, the Maxwell relaxation time (which is associated to the viscoelastic properties of the fluid) and the structure relaxation time (which is a structure build-up time). The third non-dimensional number (A) is a relationship between the kinetic and viscous processes for structure breakdown (destruction function) and the structural recovery time. The fourth group (B) is the ratio of the viscosities at low and high shear rates. This group is a measure of the shear-thinning properties and thickening behavior. Finally the last group can be interpreted as the square ratio of two geometrical mean relaxation times, so dimensionless. The next group is the pulsating Weissenberg number, which is a product between is a product of the Reynolds Number and Weissenberg numbers. The flow enhancement is calculated from equation (1-5) for different conditions in the dimensionless groups.

## 6. RESULTS AND DISCUSSION

The flow enhancement integral equation (2) was solved numerically by using na quadrature Gaussian method combined with a Lagrange method to extrapolate to zero wesh size. Withour loss of generality, in all calculations teh amplitude of the oscillations is set to one.

Predictions for the flow curve under steady shear flow have been reported elsewhere, Herrera et al., 2009. First ans second Newtonian plateaus are predicted as well as na intermediate power law region.



**Figure 1.** Flow enhancement versus dimensionless wall stress for various values of the parameter A: (i) 0.01, (ii) 0.1, and (iv) 10. Inset: flow enhancement in the region of small wall stresses, We = 10 and B = 7.

In Figure 1, the flow enhancement versus wall stress for different values of the dimensionless number A is shown. The other parameter employed in the simulations are We = 10 and B = 7. To analyze systematically the effect of the thixotropy, the value of the kinetic constant is changed to  $k=G_0^{-1}$ , enabling A to be ratio  $A=\eta_0G_0^{-1}/\lambda$ . When the value of A is in the range [0,1], the structure does not recover during the deformation period and hence the resonance curves are dramatically shifted due to the evolution of the system structure. Nevertheless, the magnitude of the maxima and minima is the same for all curves. The shifting implies that for a thixotropic fluid, the system needs more energy to obtain the same flow enhancement. In contrast, when the value of A lies in the range of [1,10], the structure recovers quickly and the curves are shifted to lower wall stresses.

In Figure 2, predictions of the flow enhancement  $(I\varepsilon^{-2})$  versus wall stress using viscometric data of CTAT at different concentrations  $(T = 30^{\circ}C)$ , are plotted (Herrera et al. 2009, 2010). For the solution with 5 wt. % CTAT (see inset) the flow enhancement increases and for  $1.2 < \tau_w < 1.5$  a drastic enhancement is observed with a maximum in the resonance curve of  $I\varepsilon^{-2} = 43.25$  at  $\tau_w = 1.4$ . In this region, the fluid experiences a pronounced shear-thinning behavior. The maximum flow enhancement is found for the 5 wt.% CTAT content, it has been reported by several authors that the shear thinning effect is responsible of the flow enhancement as reported in the literature. Nevertheless, the 5 wt. % solution has the minimum shear thinning effect, related to the value of the dimensionless B number (see Table 2 of refs 1-2). Thixotropy was found to have a negative effect on the flow enhancement, thus the maximum concentration

of CTAT shares the maximum thixotropy value (thixotropy is related to the dimensionless number A, see Table 2) and so the flow enhancement decreases due to high thixotropy. This is believed to be the cause of the maximum flow enhancement at the minimum CTAT content.

For a CTAT content of 10 wt. % the maximum in the curve is  $I\varepsilon^{-2} = 7.44$  at  $\tau_w = 5.2$ . For the 15 wt. % ssolution, the maximum in the curve is  $I\varepsilon^{-2} = 4.24$  at  $\tau_w = 2.8$ , lower than that at 10 wt. %. Finally, for a CTAT content of 20 wt.%, the maximum in the curve is  $I\varepsilon^{-2} = 4.45$  at  $\tau_w = 12.2$ . Despite that the solution is structured (A= 0.0024), this structure is destroyed by flow exhibited by the pronounced shear thinning. Furthermore, the maximum is shifted to larger wall stresses, implying a larger energy requirement for flow enhancement.



Figure 2. Flow enhancement versus dimensionless wall stress for a 5 wt. % CTAT solution at T = 30 °C. In the inset, (i) 10 wt. %, (ii) 15 wt. %, (iii) 20 wt. %. Non dimensional numbers used are reported in ref. [1-2]

#### 7. CONCLUSIONS

In this work, the rectilinear Poiseuille flow of a yield stress liquid flowing in a vibration pipe coupled with a pulsating-time pressure gradient is presented for a general class of pressure gradient noises. The structural liquid was characterized by the BMP equation which couples a time-dependent equation for the structure changes with the upper-convected Maxwell constitutive equation. The evolution equation for the structural changes was conceived to account for the kinetic process of breakage and reformation of the micelles under flow.

The following conclusions are highlighted:

The flow enhancement and power requirement for the BMP model (equations (25, 27) can be separated into two contributions, inelastic and elastic and is a function of the amplitude of the oscillations, perturbation parameter and  $W_e$  (all squared), and the dimensionless numbers A and B (representing viscoelastic, kinetic and structural effects). A necessary condition to obtain a positive flow enhancement in a structural liquid is that the fluid experiments undergoes transition from a high structured state to a less structured one induced by, i.e.  $B = \eta_0 \eta_{\infty}^{-1} >> 1$ . The viscoelastic, kinetic and structural mechanisms in the BMP model were characterized by associating non-dimensional numbers to each mechanism:

(i) 
$$A = \frac{k\eta_0}{\lambda}$$
, (ii)  $B = \eta_0 \eta_{\infty}^{-1}$  and (iii)  $We = \omega \eta_0 G_0^{-1}$ . The first one is associated to the kinetic, viscous, and structural process and the second one to the level of the structure in the liquid. The third

and structural process and the second one to the level of the structure in the liquid. The third group is the pulsating Weissenberg number which is a measure of the system viscoelasticity.

In a complex liquid, thixotropy can be interpreted as a particular case of the rupture and structural mechanisms in the system, i.e.  $De=\lambda_0\lambda^{-1} \subset A=k\eta_0\lambda^{-1}$ , when the kinetic constant is identify as a normalized constant for the shear stress, i.e.  $k=G_0^{-1}$ . The flow enhancement is a function of the concentration of the solution, in this case CTAT. In most cases, the flow enhancement decreases when the concentration of the solution increases, because the structural process dominates over the viscoelastic contribution and this is related to tthixotropy. Qualitatively, the flow enhancement for CTAT solution increases with the non-dimensional frequency according to  $I_1 \cong \left(\frac{\omega_1^*}{\omega_0^*}\right)^2 I_0$  (when the elastic effects are neglected). On the other hand, when the elastic force

are dominates, the flow enhancement follows the relationship  $I_1 \cong \left(\frac{\omega_1^*}{\omega_0^*}\right)^4 I_0$ , where  $I_0$ ,  $I_1$  are the flow enhancement calculated at frequency  $\omega_0^*$  and  $\omega_1^* = N\omega_0^*$  ( $N \in R^+$ )

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# Yield stress of a complex liquid

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#### Abstract

In the present work, the yield stress of a complex liquid is analyzed and modeled using the Bautista-Manero-Puig (BMP) constitutive equation, consisting on the Upper-Convected Maxwell equation coupled to a kinetic equation to account for the breakdown and reformation of the fluid structure. The yield stress phenomenon occurs when the shear stress becomes independent of the shear strain and the system behaves as a solid. However, when the stress overcomes the critical point (yield stress), the material begins to flow. This behavior depends on the structural, kinetics and the viscoelastic fluid properties which are analyzed here through dimensionless parameters associated to each mechanism. BMP model predictions for a complex fluid in two different flow situations are analyzed (steady state flow and Poiseuille flow). It is shown that one of the main advantages of the BMP model is that yield stress phenomenon is a natural consequence of the model when the fluidity is zero (infinity fluid viscosity), thus yield stress critical point is not forced artificially in the model equations as it is the case for other rheological models.

## **1. INTRODUCTION**

A viscoplastic material exhibits little or no deformation up to a critical value of stress which is called the yield stress. Above the yield stress, the material flows. Concentrated suspensions of solid particles in Newtonian liquids show yield stress followed by nearly Newtonian behavior. These materials are often called Bingham Plastics. Various fluids of a practical interest, such as liquid foams, paintings, droplet emulsions or high cholesterol blood, present such elastoviscoplastic behavior.

Constitutive equations that take into account the build-up and break down kinetics of a complex fluid structure during flow have been used to model several complex systems (Manero et al., 2002). Complex systems include worm-like micellar polymer solutions which are used as rheological modifiers in coating process, thin film and also in recovery oil operations. These fluids are characterized by an entangled network of large worm-like micelle structures which break down and reform during flow, exhibiting variable and rich rheological behavior. Predictions of the flow behavior of these fluids by constitutive equations have been a challenging issue (Manero et al., 2002). These systems exhibit Maxwell-type behavior in small-amplitude oscillatory shear flow and saturation of the shear stress in steady simple shear, which leads to shear banding flow (Manero et al., 2002). In the non-linear viscoelastic regime, elongated micellar solutions also exhibit remarkable features, such as the presence of a stress plateau in steady shear flow past a critical shear rate accompanied by slow transients to reach steady state <sup>(</sup>Manero et al., 2002). In view of the potential technological applications in polymer process of nanocomposites (extrusion) and oil recovery operations is surprising that the rheological modeling of yield stress in complex fluids, such as viscoelastic surfactants (or wormlike micellar systems) have not been treated amply in the current literature. There are still open questions and lack of theoretical and experimental studies with complex fluids phenomena such as thixotropy, rheopexy, shear-banding etc. They represent a challenge for new constitutive equations and this aspect motivates the present work.

## 2. DIMENSIONLESS VARIABLES, GROUPS AND EQUATIONS

#### 2.1 Non-dimensional variables

To simplify the momentum and rheological equations, the following dimensionless variables for the shear-stress, first and second normal stress differences, shear-rate, viscosity function and axial length are proposed.

$$\sigma^* = k\sigma; \quad D^* = k D; \quad \nabla^* = a\nabla; \quad r^* = r/a; \quad t^* = t/\lambda; \quad \nabla^* p^* = ka \nabla p \tag{1}$$

In (1), the characteristic time  $\lambda$  is given by the inverse of the kinetic process. The characteristic scale time **t** is the structural build time and finally **a** is the characteristic length scale in our system. The election of this particular characteristic stress (1/k) and the structural relaxation time enables the comparison with other characteristic parameters associated to physical mechanisms (viscoelastic, elastic and relaxation mechanisms, Herrera et al. 2009, 2010).

## 2.1 Non-dimensional groups

Using (1) the non-dimensionless components of the momentum, continuity and constitutive equations are obtained. In addition, the following non-dimensional groups are defined:

$$\operatorname{Re} = \frac{\rho(a\lambda^{-1})a}{\eta_0}; \ k^* = \frac{1/k}{G_0}; \ A_0 = \frac{\lambda}{t_{r0}} = \frac{\lambda}{k\eta_0}; \ A_{\infty} = \frac{\lambda}{t_{r\infty}} = \frac{\lambda}{k\eta_{\infty}}; \ A_{SB} = \frac{9}{\lambda}$$
(2)

The first group in (2) is the dimensionless Reynolds number which relates the inertial and viscous mechanisms,  $k^*$  is a ratio between the inverse of the kinetic processes and the elastic forces  $\{A_0, A_\infty\}$  can be interpreted as Deborah number and the last numbers is associate to the shear banding and structural mechanism in the system. (Herrera et al., 2009, 2010; Calderas et al., 2009).

# 3. DIMENSIONLESS EQUATION

$$A_0^{-1} \operatorname{Re} \frac{\mathrm{DV}^*}{\mathrm{Dt}^*} = -\nabla P^* + \nabla \cdot \sigma^* + \mathbf{f}^*$$
(3)

$$\boldsymbol{\sigma}^* + k^{*-1} \boldsymbol{\eta}^* \left( II_{\boldsymbol{D}^*} \right) \boldsymbol{\sigma}^* = 2 \boldsymbol{\eta}^* \left( II_{\boldsymbol{D}^*} \right) \boldsymbol{D}^*$$
(4)

$$\frac{d}{dt^*}Ln\eta^*\left(II_{\mathbf{D}^*}\right) = 1 - \varphi_0^*\eta^*\left(II_{\mathbf{D}^*}\right) + \left(1 + A_{SB}II_{\mathbf{D}^*}\right)\left(1 - \varphi_\infty^*\eta^*\left(II_{\mathbf{D}^*}\right)\right)\sigma^*: \mathbf{D}^*$$
(5)

These equations are completed by some suitable initial and boundary conditions in order to solve the system. For instance, the initial conditions  $\sigma^*(t) = \sigma_0^*$  and  $V^*(t^*) = V_0$  and the boundary condition  $V^* = V_{\Gamma}^*$  on the boundary  $\partial \Omega$  are convenient. In steady state the BMP model takes the following equation

$$\eta^{*-1} (\Pi_{\mathbf{D}^{*}}) \boldsymbol{\sigma}^{*} + \mathbf{k}^{*-1} \boldsymbol{\sigma}^{*} = 2\mathbf{D}^{*}; \ \eta^{*-1} (\Pi_{\mathbf{D}^{*}}) = \frac{\varphi_{0}^{*} + \varphi_{\infty}^{*} (1 + \mathbf{A}_{SB} \Pi_{\mathbf{D}^{*}}) \boldsymbol{\sigma}^{*} : \mathbf{D}^{*}}{1 + (1 + \mathbf{A}_{SB} \Pi_{\mathbf{D}^{*}}) \boldsymbol{\sigma}^{*} : \mathbf{D}^{*}}$$
(6)

In the rest of this paper, the constitutive equation given in (18) is used to predict the flow behavior and yields stress of a structural liquid. The non-dimensional momentum and constitutive equations given by equations (3-6), will be used in the following flow situations: a) Steady state shear flow and b) Poiseuille flow

## **3. RHEOMETRIC FLOWS**

#### 3.1 Unsteady state shear flow

$$\nabla^* \mathbf{V}^* = \gamma^* \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix}; \boldsymbol{\sigma}^* = \begin{pmatrix} \sigma_{rr}^* & 0 & \sigma_{rz}^* \\ 0 & \sigma_{\theta\theta}^* & 0 \\ \sigma_{zr}^* & 0 & \sigma_{zz}^* \end{pmatrix}; \ 2\mathbf{D}^* = \gamma^* \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix}$$
(7)

The shear stress is given by the following equation:

$$\sigma_{rz}^{*} \begin{pmatrix} \sigma_{rz}^{*} \end{pmatrix} = \eta^{*} \begin{pmatrix} \sigma_{rz}^{*} \end{pmatrix} = \frac{\gamma^{*2} - \phi_{0}^{*} + \sqrt{\left(\gamma^{*2} - \phi_{0}^{*}\right)^{2} + 4\phi_{\infty}^{*} \gamma^{*2}}}{2\phi_{\infty}^{*} \gamma^{*}}$$
(8)

Where  $\phi_0^* = \frac{\phi_0}{k\lambda^{-1}}$  and  $\phi_\infty^* = \frac{\phi_\infty}{k\lambda^{-1}}$  can be interpreted as a fluidities to low and high shear rate respectively. When the shear rate is of the order of  $\dot{\gamma}_{rz}^* \rightarrow \sqrt{A_0}$ , equation (8) takes the following form:

$$\operatorname{Lim}_{\operatorname{d}^{*}_{\gamma \to \sqrt{\varphi_{0}^{*}}}} \sigma_{\operatorname{zr}}^{*} \left( \begin{array}{c} \gamma \\ \gamma \end{array} \right) = \sigma_{\operatorname{ys}}^{*} = 1/\sqrt{\varphi_{\infty}^{*}}; \quad \operatorname{Lim}_{\operatorname{d}^{*}_{\gamma \to \sqrt{A_{0}}}} \eta^{*} \left( \begin{array}{c} \gamma \\ \gamma \end{array} \right) = \frac{1/\sqrt{A_{\infty}}}{\gamma}$$
(9)

In equation (9)  $\sigma_{y_s}^* = 1/\sqrt{\phi_{\infty}^*}$  is the yield stress of the BMP model and  $A_{\infty} = (\lambda/k) \phi \infty$  is related to the kinetics, structural and viscous mechanisms to high shear rate.

$$\operatorname{Lim}_{{}_{\stackrel{\circ}{\gamma}\to\infty}} \sigma_{zr}^{*} \begin{pmatrix} {}_{\stackrel{\circ}{\gamma}} \end{pmatrix} = {}_{\stackrel{\circ}{\gamma}}^{*}; \qquad \qquad \operatorname{Lim}_{{}_{\stackrel{\circ}{\gamma}\to\infty}} \eta^{*} \begin{pmatrix} {}_{\stackrel{\circ}{\gamma}} \end{pmatrix} = 1 \qquad (10)$$

#### **3.2 Poiseuille flow**

#### 3.2.1 Axial velocity

The non dimensional axial velocity for the BMP model is obtained:

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$$V_{z}^{*}(\mathbf{r}^{*}) = \frac{1}{4A_{0}\sigma_{w}^{*}} \left\{ \sigma_{w}^{*2}(\mathbf{r}^{*2}-1) + \sqrt{\left(\sigma_{w}^{*2}\mathbf{r}^{*2}-\phi_{\infty}^{*}\right)^{2} + 4\sigma_{w}^{*2}\mathbf{r}^{*2}\phi_{0}^{*}} - \sqrt{\left(\sigma_{w}^{*2}-\phi_{\infty}^{*}\right)^{2} + 4\sigma_{w}^{*2}\phi_{0}^{*}} + 3A_{\infty}Ln\phi_{\infty}^{*}\left(\sigma_{w}^{*2}\mathbf{r}^{*2}-\sigma_{w}^{*2}\right) + \Theta_{1}\left[\mathbf{r}^{*},\sigma_{w}^{*},\phi_{0}^{*},\phi_{0}^{*}\right] + G_{2}\left[\mathbf{r}^{*},\phi_{w}^{*},\phi_{0}^{*},\phi_{0}^{*}\right] \right\}$$
(11)

Where the functions G1 and G2 are given by:

$$G_{1}\left[z,\sigma_{w}^{*},\phi_{0}^{*},\phi_{\infty}^{*}\right] = Ln \begin{vmatrix} \frac{2A_{0}-\phi_{\infty}^{*}+\sigma_{w}^{*2}r^{*2}+\sqrt{(\sigma_{w}^{*2}r^{*2}-\phi_{\infty}^{*})^{2}+4\sigma_{w}^{*2}r^{*2}\phi_{0}^{*}}}{2A_{0}-\phi_{\infty}^{*}+\sigma_{w}^{*2}+\sqrt{(\sigma_{w}^{*2}-\phi_{\infty}^{*})^{2}+4\sigma_{w}^{*2}\phi_{0}^{*}}} \end{vmatrix} 2^{A-B} \\ \int \frac{(12)}{\sqrt{(12)}} \\ G_{2}\left[z,\sigma_{w}^{*},\phi_{0}^{*},\phi_{\infty}^{*}\right] = Ln \begin{vmatrix} \frac{\phi_{\infty}^{*2}+(2\phi_{0}^{*}-\phi_{\infty}^{*})\sigma_{w}^{*2}+\sqrt{(\sigma_{w}^{*2}-\phi_{\infty}^{*})^{2}+4\sigma_{w}^{*2}\phi_{0}^{*}}}{\phi_{\infty}^{*2}+(2\phi_{0}^{*}-\phi_{\infty}^{*})\sigma_{w}^{*2}r^{*2}+\sqrt{(\sigma_{w}^{*2}r^{*2}-\phi_{\infty}^{*})^{2}+4\sigma_{w}^{*2}r^{*2}\phi_{0}^{*}}} \end{vmatrix} \end{vmatrix}$$

## 3.2.2 Volumetric flow

The volumetric flow rate may be calculated from the general integral expression:  

$$Q^{*} = \frac{Q}{a^{3}/\lambda} = \int_{0}^{2\pi} \int_{0}^{1} \gamma_{rz}^{*} r^{*2} dr^{*} d\theta \xrightarrow{\text{After Integration}} Q^{*} = -\pi \int_{0}^{1} \gamma_{rz}^{*} r^{*2} dr^{*}$$
(14)

Substitution of axial velocity (Equations 11-13) into the equation (14), the following expression for the volumetric flow is obtained:

$$Q^{*} = \frac{\pi}{4\phi_{0}^{*}\sigma_{w}^{*3}} \begin{cases} \phi_{\infty}^{*}\sigma_{w}^{*2} - \frac{\sigma_{w}^{*4}}{2} + \frac{1}{2}\phi_{\infty}^{*}\left(2\phi_{0}^{*} - \phi_{\infty}^{*}\right) - \frac{1}{2}\left(\sigma_{w}^{*2} + \left(2\phi_{0}^{*} - \phi_{\infty}^{*}\right)\right)\sqrt{\left(\sigma_{w}^{*2} - \phi_{\infty}^{*}\right)^{2} + 4\phi_{0}^{*}\sigma_{w}^{*2}} \\ + 2\phi_{0}^{*}\left(\phi_{\infty}^{*} - \phi_{0}^{*}\right)\log\left[\frac{2\phi_{0}^{*}}{\left(2\phi_{0}^{*} - \phi_{\infty}^{*}\right) + \sigma_{w}^{*2} + \sqrt{\left(\sigma_{w}^{*2} - \phi_{\infty}^{*}\right)^{2} + 4\phi_{0}^{*}\sigma_{w}^{*2}}}\right] \end{cases}$$
(15)

# 3.2.3 Power requirement

The power requirement per unit length  $P=2\sigma_{w}^{*}Q^{*}$  is easy calculated from equation (15), and is given by:

$$P\left(\sigma_{w}^{*};\phi_{0}^{*},\phi_{\infty}^{*}\right) = \frac{\pi}{2\phi_{0}^{*}\sigma_{w}^{*2}} \begin{cases} \phi_{\infty}^{*}\sigma_{w}^{*2} - \frac{\sigma_{w}^{*4}}{2} + \frac{1}{2}\phi_{\infty}^{*}\left(2\phi_{0}^{*}-\phi_{\infty}^{*}\right) - \frac{1}{2}\left(\sigma_{w}^{*2} + \left(2\phi_{0}^{*}-\phi_{\infty}^{*}\right)\right)\sqrt{\left(\sigma_{w}^{*2}-\phi_{\infty}^{*}\right)^{2} + 4\phi_{0}^{*}\sigma_{w}^{*2}} \\ + 2\phi_{0}^{*}\left(\phi_{\infty}^{*}-\phi_{0}^{*}\right)\log\left[\frac{2\phi_{0}^{*}}{\left(2\phi_{0}^{*}-\phi_{\infty}^{*}\right) + \sigma_{w}^{*2} + \sqrt{\left(\sigma_{w}^{*2}-\phi_{\infty}^{*}\right)^{2} + 4\phi_{0}^{*}\sigma_{w}^{*2}}} \right] \end{cases}$$

In terms of the dimensionless velocity, the volumetric flow and the power requirements are nonlineal functions of the wall stress and they are governed by the structural, kinetics and shearthinning or shear thickening behavior through dimensionless characteristic numbers.

# **3.2.3 Capillary viscosity**

From volumetric flow, is easy to calculate the capillary viscosity:

$$\eta^* \begin{pmatrix} \sigma^* \\ \gamma_w \end{pmatrix} = \frac{\sigma^*_w}{\sigma^*}; \quad \gamma^*_w = \gamma^*_{zr} \Big|_{r^*=1} = \frac{1}{\pi \sigma^{2^*}_w} \frac{d}{d\sigma^*_w} \left(\sigma^{3^*}_w Q^*\right) = \frac{1}{\sigma^*_w} \frac{d}{d\sigma^{2^*}_w} \left(\frac{2\sigma^{3^*}_w Q^*}{\pi}\right)$$
(16)

Where the shear strain at the wall is given by the well-known Rabinovich equation:

$$\begin{bmatrix} \sigma_{w}^{*} = \sigma_{zr}^{*} \\ r_{w}^{*} = \gamma_{zr} \end{bmatrix}_{r^{*}=1}^{*} = -\frac{1}{\pi \sigma_{w}^{2^{*}}} \frac{d}{d\sigma_{w}^{*}} \left(\sigma_{w}^{3^{*}} Q^{*}\right) = -\frac{1}{\sigma_{w}^{*}} \frac{d}{d\sigma_{w}^{2^{*}}} \left(\frac{2\sigma_{w}^{3^{*}} Q^{*}}{\pi}\right)$$
(17)

Finally, the expression for the viscosity at the capillary is given by:  $\eta^* \begin{pmatrix} \Box^* \\ \gamma_w \end{pmatrix} = \frac{2A_0 \sigma_w^{2^*}}{\sigma_w^{2^*} - A_\infty + \sqrt{(\sigma_w^{2^*} - A_\infty)^2 + 4A_0 \sigma_w^{*2}}}$ (18)

Finally equation (19) represents the viscosity in the capillary. This expression depends on the dimensionless number associated to the kinetics, structural mechanisms and the wall stress.

# 4. RESULTS AND DISCUSSION







Figure 2. Dimensionless shear viscosity vs shear strain as a function of the dimensionless number A0 : Inset the dimensional material properties used in the simulation.



Figure 3. Axial velocity as a function of the dimensionless number A0. The parameters used in the simulations are the same employed in the Figs. 1-2.

In figure 1, the shear stress of the BMP model as a function of the shear strain for different values of the dimensionless number  $A_0$  is shown on a linear scale. It is important to note that at low values of  $A_0$ , an apparent yields stress is observed (curves corresponding to III, IV, V values). When the dimensionless number  $A_0$  goes to zero, the value of the shear stress is equal to the true yield stress,  $1/\sqrt{A_{\infty}}$  which corresponds exactly to a value of zero fluidity or infinite viscosity.

In figure 2, it is plotted the dimensionless viscosity as a function of the shear strain for different value of dimensionless number A0. In all case the behavior is the similar the only different is the value of the plateau given by:  $1/\sqrt{A_{\infty}}$ . The value of this plateau is governed by the inverse of the dimensionless number  $A_{\infty}$ , i.e., the ratio between two characteristic times the structural relation times and the rupture time to high shear rate. Except case a when the system is independent of the shear strain in all range of deformation, the case b-d show a similar behavior. To low shear rate, the systems b-d a Newtonian plateau, follows a shear thinning behavior for a critical shear rate, follows of a constant behavior for shear strain larger than 100 s<sup>-1</sup>. The line e shows a real Bingham plastic behavior according to the BMP model. In this point, the BMP model predicts a yield stress of the order of  $10^5 \text{ s}^{-1}$ , for a lower shear rate close  $10^3 \text{ s}^{-1}$ . In a log-log simulation, the line predicts a lineal behavior with a slope -1 and abscise of the Ln  $|1/\sqrt{A_{\infty}}|$ . Physically, the value of the plateau depends on the kinetics, structural and viscoelastic mechanism to high shear rate through dimensionless number  $A_{\infty}$ .

In figure 3 it is plotted axial velocity in our capillary as a function of the radial position for different value of the dimensionless number  $A_{\infty}$ . In all simulations (a-d) the shape of the velocity is a parabolic. However, when the dimensionless number  $A_{\infty}$  goes to zero (infinitive viscosity or fluidity zero) the shape of the form is parabolic but the maximum velocity decrease. For a critical value of the dimensionless number  $A_{\infty}$ , the parabolic form of the velocity decrease and the system presents a homogeneous flow, i.e., in this system the velocity is independent of the position (d, e). From a macroscopic point of view, the system present a maximum in its viscosity, from a microscopic point of view the numbers of links, bonds or entanglement is maximum.

#### **5. CONCLUSIONS**

In this work, a comparison between deferent constitutive equation that describes the Yield Stress presents in complex system that presents change in its structure. The e complex liquid was characterized by the BMP equation which couples a time-dependent equation for the structure changes with the Upper-Convected Maxwell constitutive equation. The evolution equation for the structural changes was conceived to account for the kinetic process of breakage and reformation under flow. The BMP model is compare with others viscoplastic and viscoplastic models and the following conclusions are reached:

• According to the BMP constitutive equation, the viscoelastic, kinetic and structural mechanisms in the BMP model were characterized by the association of non-dimensional

numbers to each mechanism: (i)  $\phi_0^* = \frac{\phi_0}{k/\lambda}$ , (ii)  $\phi_\infty^* = \frac{\phi_\infty}{k/\lambda}$ . One of them associated to the kinetic, viscous and structural process and the second one to the level of the structure in the system. In particular, when the kinetic constant (k) is  $_{k=G_0^{-1}}$  the number A reduces to the Deborah number which is a measure of the thixotropy effects in the system.

- The yield stress of the BMP model is given by:  $\sigma_{ys}=1/\sqrt{\phi_{\infty}^*}$ , i.e., the Yield stress is given by the structural, kinetics and viscoelastic mechanism to high shear rate. In terms of the dimensionless numbers is the inverse of the square of the Deborah number to high shear rates.
- When the kinetic constant k is identify as a normalized constant by the shear stress, i.e., the Yields Stress is given by the inverse of the square root of the Weissenberg number, i.e., σ<sub>vs</sub>=1/√φ<sub>∞</sub><sup>\*</sup>
- The Yield Stress in the BMP model is a natural consequence of the model in the zone where the shear stress is independent of the shear strain, in contrast with the others model that propose in where the Yield Stress is added.

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# SYNTHESIS OF PPY-TIO PLASMA COMPOSITES

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In this work, layers of polypyrrole (PPy) combined with titanium oxide particles were synthesized by plasma with the purpose to have the properties of both materials, photoactivity of TiO and hydrophylicity and electric semi-conductivity of PPy. These combinations have potential application in the sorption of water pollutants and in the synthesis of photo-conductive polymers. The syntheses combined simultaneous degradation of tetrapropoxide of titanium and polymerization of pyrrole developed with electrical, rf, resistive, low-pressure, glow discharges. The PPy-TiO composites are formed with TiO particles dispersed in layers of PPy. The TiO particles have agglomerates in several morphologies with characteristic length from 360 to 800 nm. Conductivity of composites was calculated in the interval of  $10^{-5}$  to  $10^{-8} \Omega^{-1} \cdot m^{-1}$ .

# SYNTHESIS OF BIFUNCTIONAL MONOMERS STYRENE DERIVATIVES

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# Abstract

Grignard reagents have proven to be widely used and usedfull as synthetic tool and are the most widely employed organometallic reagent. This article describes the organic synthesis of bifunctional monomer derived from styrene by a Grignard reaction with aldehydes and ketones. The Grignard reagent was synthesized from 4-bromostyrene and magnesium in THF. The magnesium was activated by adding to the reaction a small amount of iodine. At the end of the synthesis were obtained four different bifunctional monomers having two terminal substituents, a vinyl group and a group-OH. These monomers were obtained with a high yield from a solution of Mg and iodine.

# Introduction

Bifunctional monomers have two terminal reactive sites which can be used for the design of structures, controlled molecular weights, well-defined architectures and end groups combined. The incorporation of functional groups within the polymer chain, can greatly improve properties such as hydrophilicity, hydrophobicity, biocompatibility, adhesion, etc.., providing polymers with useful features. When a monomer contains two chemically different functional groups, one of them can be selectively polymerized under certain conditions, without interference from the other functional group. It has carried out the synthesis of polymers using bifunctional monomers from living polymerization methods. <sup>[1, 2]</sup> Zhang and Ruckenstein<sup>[3]</sup> synthesized a bifunctional monomer 4-(vinylphenyl)-1-butene by a coupling reaction between vinylbenzyl chloride and alquilmagnesium chloride and subsequently held an anionic polymerization the C = C double bond of styrene, generating a polymer with a polystyrene chain butenyl side chains.

Bifunctional monomers styrene derivatives synthesized in this work, have a vinyl group and an OH group, the vinyl group can be polymerized by any polymerization method with a variety of monomers, in the case of alcohol, it can react with alkylene oxides (propylene oxide, ethylene oxide, butylene oxide), plus a variety of isocyanates, obtaining different types of polyurethanes.<sup>[4]</sup> The bifunctional monomers can be synthesized from a Grignard reaction<sup>[5-13]</sup>, obtaining a monomer with two terminal functional substituents.

In this paper we report the production of bifunctional monomers styrene derivatives through synthesis of a Grignard reagent from 4-bromoestireno and magnesium, iodine using activated magnesium in THF. This Grignard reagent was reacted with four different compounds containing carbonyl groups, acetophenone, methyl ethyl ketone, butyraldehyde and benzaldehyde.

# Experimental

# Chemicals

THF (Aldrich) was distillated with sodium, 2-butanone (methyl ethyl ketone, MEK) (Aldrich 99%) was distillated over MgSO<sub>4</sub>. Acetophenone (Aldrich 99%) distillated under reduced pressure at 2 mmHg over MgSO<sub>4</sub>. Benzaldehyde (Aldrich 99%) was washed with NaOH to decrease  $CO_2$  and then washed with a saturated solution of Na<sub>2</sub>SO<sub>3</sub> and water, finally distilled

under reduced pressure of 2 mmHg over MgSO<sub>4</sub>. Butyraldehyde (Aldrich 99%) purified by fractional distillation over CaCl<sub>2</sub>. Ethyl ether (Aldrich) was distillated with sodium, anhydrous iodine (Aldrich 99%) with less than 100 ppm of H<sub>2</sub>O, magnesium power -50 messh (Aldrich 99%), 4-Bromoestireno (AmfineCom 98%) was used without further purification. HCl solution at 37% (w/w) Aldrich.

# Synthesis of the Grignard reagent of (4-vinylphenyl) magnesium bromide

The reagent preparation was carried out in a 250 mL 3-neck flask with a magnetic stirrer which was added 1.59 g (65.55 mmol) of magnesium, a condenser and an addition funnel. The system was flamed with vacumm (1mmHg) and filled with argon (Ultra high Purity grade), then the magnesium was activated by adding a few crystals of I<sub>2</sub> and 10 mL of THF were added with constant stirring. Few drops of 4-bromostyrene were added and exothermic reaction can be registered, followed, the remaining 10 g (54.63 mmol) of 4-bromostyrene were added with a dropping funel, the feeding rate is used to control the reaction temperature that cannot reach more than 35 ° C to prevent polymerization. The reaction mixture was allowed to react for 4 h in an inert atmosphere at room temperature.

# Grignard reaction with aldehydes and ketones groups

The Grignard reaction was carried out in situ, so that after the reaction time for the formation of the Grignard reagent was added dropwise a solution of 51.90 mmol of aldehyde or ketone in 20 mL of dry THF at room temperature, the mixture of Grignard reagent with the carbonyl group was allowed to reflux overnight under an inert atmosphere. The reaction was monitored by gas chromatography-mass spectroscopy. It carries out the extraction of the reaction using a solution of 10% HCl and ethyl ether in a separating funnel. Then the organic extraction is dried with MgSO<sub>4</sub> by vigorously stirring. Finally the product is filtered and concentrated by evaporation. (**Figure 1**)



**Figure 1.** Grignard Reaction with aldehydes and ketones groups <sup>[14,15]</sup>

# Analysis

The characterization of related compounds was determined by a NMR (500 MHz) spectrophotometer Brucker ADVANCED III. Chemical shifts were expressed in parts per million. FT-IR spectra were taken with a Nicolet Magna 550 Infrared spectrophotometer equipped with an optical interferometer of potassium bromide. The mass spectra GC / MS were obtained using a gas chromatograph VARIAN CP 3800, with a mass spectrum VARIAN 2000, which analyzes masses of 50 to 300 m / z. The oven temperature was maintained at 80 ° C for 2 minutes, then raise to 10 ° C / min up to 230 ° C, when this temperature is reached, it is maintained isothermally for 15 minutes giving a total analysis time of 32 minutes.

# **Results and Discussion**

4-vinylphenyl magnesium bromide was prepared through the reaction of 4-bromostyrene with

magnesium after 4 h of reaction (**Figure 2**). An important aspect of this reaction is the amount of magnesium used, an excess of magnesium can lead to reduction of the ketone during the condensation step, carrying out pinacol reaction, which produces a solid derivative of magnesium which is decomposed by hydrolysis in a magnesium salt and pinacol <sup>[16]</sup>. Is important to consider that with this methodology several molar rations between the reagents have adjusted and a high purity monomers are obtained, avoiding the purification step.



Figure 2. Synthesis of the Grignard reagent of (4-vinylphenyl) magnesium bromide

Once the Grignard reagent were prepared, addition reaction to a carbonyl group (butyraldehyde, benzaldehyde, MEK, acetophenone) was carryout in THF, taking care not to raise the temperature above 35 ° C, for the reason mentioned, the reaction was left overnight in an inert atmosphere. (**Figure 2**) The reaction solution obtained in all cases had a dark red-brown, and almost complete consumption of the carbonyl compound. The yield obtained after extraction of the reactions was determined gravimetrically (**Table 1**), obtaining bifunctional monomers with secondary and tertiary alcohols.

Group	Bifunctional Monomer	Identification	Molar Ratio	Yield
			Mg:X:CO	(%)
Butiraldehyde	1 - (4-vinylphenyl)-butane-1-ol	VF-I	1.0:1.0:1.0	84.3
Benzaldehyde	Phenyl (4-vinylphenyl) methanol	VF-II	1.2:1.0:0.95	86.8
MEK	2 - (4-vinylphenyl) butane-2-ol	VF-III	1.2:1.0:0.95	91.1
Acetophenone	1-phenyl-1-(4-vinylphenyl) ethanol	VF-IV	1.2:1.0:0.95	71.7

**Table 1.** Grignard reaction with aldehydes and ketones in dry THF.

The characterization by FT-IR show bands characteristic of these bifunctional monomers. The presence of the band attributed to the stretching O-H of the alcohols in 3300 - 3400 cm<sup>-1</sup>, as well as the stretching of the C = C of the vinyl in 1688 -1568 cm<sup>-1</sup>, and the flexions at 700 - 1000 cm<sup>-1</sup> corresponding to aromatic bending of C-H bond of the ring.. Further characterization by FT-IR where the groups were observed for each bifunctional monomer, were also analyzed by GC/MS, <sup>1</sup>H and <sup>13</sup>C NMR.

In the analysis by GC-MS, we observed two patterns of behavior of molecules, depending if the styrene monomer substituent is an aryl group (benzaldehyde and acetophenone) or an alkyl chain (butyraldehyde and MEK). In the case of bifunctional monomers VF-I (m/z=176) and VF-III (m/z=176) containing alkyl chains as substituents, is not observed the molecular ion corresponding to the monoisotopic mass in the spectrum of masses, not so for VF-II (m/z=210) and VF-IV (m/z=224), which contain an aryl substituent, observing the molecular ion, it could be because the aryl group gives more stability to the molecule, and as a result the molecular ion could be detected.

The <sup>1</sup>H NMR spectra (**Figure 3**) corresponding to the bifunctional monomers VF-I and VF-II obtained from aldehydes show chemical shifts characteristic in both cases, show different chemical shifts depending if the substituent  $R_2$  is an aryl group or an alkyl chain. At 7.45 ppm show a complex signals, which integrates for 4H (VF-I) and 9H (VF-II) respectively. At 6.75 shows a double-doubles signal that integrates for hydrogen (Hc) of the vinyl with a coupling constant  $J_1$  11.03 Hz (cis) and  $J_2$  17.65 Hz (trans). At 5.25 ppm there is a signals system conformed by two doublets which integrates for a hydrogen respectively, hydrogen Hb (J=17.65 Hz) and hydrogen Ha (J=10-11 Hz) belonging to the vinyl hydrogens. The chemical shift corresponding to the neighbor hydrogen at OH, has different chemical shifts in both monomers, at 4.70 ppm a triplet with a J= 6.62 Hz for the VF-I (Hg) and a singlet at 5.85 ppm for the VF-II (Hf). The chemical shift corresponding to OH appears at 1.57 ppm in a broad singlet for the VF-I and at 2.25 ppm for the FV-II. Finally at 1-2 ppm are the chemical shifts corresponding to the alkyl portion of the monomer VF-I. The bifunctional monomers derived from ketones show chemical shifts similar to those obtained from aldehydes.



Figure 3. <sup>1</sup>H RMN (Advance III 500 MHz, CDCl<sub>3</sub>) for the bifunctional monomers from aldehydes groups

The characterization was completed with the spectra of <sup>13</sup>C RMN (**Figure 4**), which show a characteristic chemical shift in each monomer, at 74 ppm ( $C_g$ ) is the carbon which carries the oxygen atom which is present in each monomer, at 114 ppm and 136 ppm show the  $C_a$  and  $C_b$  carbons corresponding to the carbons of the vinyl group of the styrene.



Figure 4. <sup>13</sup>C RMN (Advance III 125.686 MHz, CDCl<sub>3</sub>) for the bifunctional monomers from aldehydes and ketones.

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# Conclusions

The synthesis of the Grignard reagent of 4-vinylphenyl magnesium bromide was reached by the reaction of 4-bromoestireno and an  $Mg/I_2$  solution in dry THF, giving better results by using a molar ratio of 1.0: 1.2 respectively where iodine crystals help to activate the magnesium surface to carry out of the Grignard reagent formation. A subsequent reaction of the Grignard reagent with aldehydes and ketones was carried out in order to obtain new C-C bonds between the carbonyl group (butyraldehyde, benzaldehyde, acetophenone and MEK) and carbon nucleophilic of the Grignard reagent of 4-vinylphenyl magnesium bromide forming an alkoxide ion which when is hydrolyzed give rise to bifunctional monomers styrene derivatives with secondary and tertiary alcohols.

The four different bifunctional monomers obtained: 1 - (4-vinylphenyl)-butane-1-ol, phenyl (4-vinylphenyl) methanol, 2 - (4-vinylphenyl) butane-2-ol and 1-phenyl-1-(4 -vinylphenyl) ethanol had yield above 80% in almost all cases, calculated by gravimetric analysis and finally their characterization by FT-IR, <sup>1</sup>H and <sup>13</sup>C NMR confirmed their synthesis.

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Bis 2-(acryloyloxyethyl) terephthalate was produced from bis (hydroxyethyl) terephthalate, BHET, and acryloyl chloride. BHET was obtained by PET glycolysis with boiling ethylene glycol, using post-consumer PET particles and zinc acetate as catalyst at atmospheric pressure.

The bis 2-(acryloyloxyethyl) terephthalate was obtained by dropwise addition of acryloyl chloride to a stirred solution of BHET in acetone using triethyl amine as catalyst, at room temperature under argon atmosphere. The product was purified and characterized by DSC, FT-IR and NMR. The cross-linking capacity of this acrylic monomer was tested in order to be used as a possible dental bonding agent.

Cross-linking was studied in bulk both thermally and photochemically. The crosslinked polymer was characterized by means of DMA, FT-IR and NMR. Results were compared with commercial monomers.

# SYNTHESIS OF ZINC OXIDE NANOPARTICLES USING BICONTINUOUS MICROEMULSIONS

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# Abstract

The synthesis of zinc oxide (ZnO) nanoparticles with high purity by precipitation from a bicontinuous microemulsion is reported in this work. The microemulsion was composed of sodium dodecylsulfate (SDS), sodium bis-2-ethylhexyl sulfosuccinate (AOT) as the surfactants,  $0.9M \text{ Zn}(NO_3)_2$  solution as the aqueous phase and toluene as the organic phase. ZnO nanoparticles with diameters between 6.0 and 22 nm were obtained by hydrolysis of Zn(NO<sub>3</sub>)<sub>2</sub> with NaOH aqueous solution and precipitation, followed by calcination of the precipitate. Higher yields and productivities of ZnO nanoparticles were obtained compared to values produced with w/o micremulsions reported in the literature. By increasing the amount of the aqueous Zn(NO<sub>3</sub>)<sub>2</sub> solution, smaller particles were obtained.

# Introduction

Different techniques for preparing ZnO nanoparticles have been investigated: chemical vapor deposition, sol-gel, chemical co-precipitation, spray pyrolysis, microemulsion precipitation obtaining. nanospheres, nanorods, nanowires, nanotubes and flower-like nanostructures [1-15]. Among these, precipitation in reverse microemulsions is a well-established technique for preparing particles with average diameters smaller than 10 nm and low particle size polydispersity. ZnO nanoparticles with average diameters around 10 nm [11-13, 15] as well as small particles ( $\approx$  150 nm) [14] have been obtained.]. Using reverse microemulsions stabilized with zinc (bis ethylhexyl) sulfosuccinate to precipitate zinc oxalate by adding oxalic acid. ZnO nanoparticles of about 5-13 nm in diameter were obtained by zinc oxalate calcination [13]. Inoguchi et al. [15] reported the preparation of spherical ZnO nanoparticles as small as 5 nm in average diameter by direct precipitation in a reverse microemulsion containing an aqueous solution of sodium hydroxide to which was added an alcoholic solution of zinc diethoxide.

In reverse microemulsion precipitation, the hydrolysis reactions take place inside the watermicroemulsion droplets suspended in a hydrophobic medium; however, this technique has the drawback that the productivity of nanoparticles is low. Some authors have employed bicontinuous microemulsions rather than w/o microemulsions because the ratio of water-to-oil is larger, which increases the productivity of metal oxide nanoparticles, keeping the typical size of nanoparticles obtained in reverse microemulsions [14, 16-18].

Here we report the synthesis of ZnO nanoparticles using bicontinuous microemulsions since they contain larger aqueous phase concentrations, where the ZnO precursor is located, than w/o microemulsions. This method allows obtaining higher yields and productivities.

# Experimental

#### Materials

Sodium dodecylsulfate (SDS), sodium bis-2-ethylhexyl sulfosuccinate (AOT) and  $Zn(NO_3)_2 \cdot 6H_2O$  were all 98% pure from Sigma-Aldrich. NaOH, 98.2 % pure (Golden Bell), and toluene, 99 % pure (Golden Bell), were used as received. De-ionized and triple-distilled water with conductivity

smaller than 6  $\mu S/cm$  was used.

# Phase diagram

The one-phase microemulsion region at the reaction temperature (70 °C) was determined by titrating solutions of AOT/SDS (2/1 by weight) in toluene at different surfactant with 0.9M  $Zn(NO_3)_2$  aqueous solution under continuous agitation. To determine the mixture compositions where bicontinuous microemulsion formed, conductivities of were analyzed with a 3173R JENCO conductivity meter at 70 °C.

# **Microemulsion precipitation**

To the microemulsion containing  $Zn(NO_3)_2$  at different feeding rates a NaOH aqueous solution was added. The total amount of NaOH added was 1.43 times the stoichiometric ratio (NaOH /Zn(NO<sub>3</sub>)<sub>2</sub>. After the addition period, the reacting system was left to stand for 30 min at the reaction temperature. The precipitate was recovered by filtration and mixed with an aqueous acetone solution (81/19 w/w) in a sonic bath for 15 minutes to remove the surfactants and nonreacted material, and centrifuged to recover the wet solids. This procedure was repeated 10 times. The residual wet solid was then dried in an oven at 60 °C and then calcinated at 400 °C for two hours in an oven.

# Nanoparticles characterization

The nanoparticles were characterized in a Siemens D-5000 X-ray diffractometer (XRD). Particle size was determined by transmission electronic microscopy (TEM) in a JEOL JEM-1010; The purity of the final product was determined by atomic absorption spectrometry using a Varian Spectra 250 AA

# **Results and Discussion**

Figure 1 shows the microemulsion region for the system containing a mixture of AOT/SDS (2/1 by weight), toluene and an 0.9M aqueous solution of  $Zn(NO_3)_2$ . Three ratios of the surfactants/toluene mixture, which allowed a high percent of aqueous solution inside the microemulsion region, were selected. To find the bicontinuous microemulsion zone, the content of the 0.9 M aqueous  $Zn(NO_3)_2$  solution was increased while maintaining the ratio of surfactant/toluene constant and their conductivity was measured.



Figure 1: Partial phase diagram obtained at 70 ° C for mixtures of toluene, AOT/SDS (2/1 w/w), and 0.9 M Zn(NO<sub>3</sub>)<sub>2</sub> aqueous solution.

The electrical conductivity as a function of the amount of the aqueous solution of  $Zn(NO_3)_2$  for the three surfactants/toluene ratios selected (50/50, 55/45 and 60/40 w/w) is shown in Figure 2. By increasing the aqueous solution content, the microemulsion conductivity increased. The percolation theory indicates that bicontinuous microemulsions have a high conductivity as a result of continuous (or connected) aqueous phase domains [19-22]. When the ratios of surfactants/toluene were 50/50 and 55/45, the conductivities were very low, which indicated that w/o microemulsions, instead of bicontinuous microemulsions were formed. However, when the surfactants/toluene ratio of 60/40 (w/w) with a percent of aqueous solutions larger than 15% were used, a big increase in conductivity was detected, reaching a maximum of 1575  $\mu$ S/cm around 27% of aqueous solution indicating bicontinuous structure.



Figure 2. Electrical conductivity of the one-phase microemulsions versus concentration of a 0.9M  $Zn(NO_3)_2$  aqueous solutions for three surfactant mixture/toluene weight ratios

ZnO nanoparticles were obtained by precipitation using 22% and 27% of 0.9 M aqueous  $Zn(NO_3)_2$  solution and a ratio of surfactants/toluene of 60/40. Table 1 shows the  $Zn(NO_3)_2$  concentrations and the dosing times used.

Sample	Zn(NO <sub>3</sub> ) <sub>2</sub> concentration (wt. %)	Dosing Time (min)	Dn (nm)	PDI	ZnO a Purity (%)	Productivity (g ZnO/100 g reaction mixture)	Yield (%)
100-1	22	100	21.74	1.10	98	1.25	98.27
125-1	22	125	18.40	1.17	99	1.13	88.83
150-1	22	150	8.74	1.38	95	1.11	87.26
100-2	27	100	7.81	1.19	99	1.30	85.30
125-2	27	125	6.00	1.21	98	1.34	87.93
150-2	27	125	6.50	1.3	96	1.36	89.24

Table 1. Dosing time and properties of ZnO nanoparticles

The X-ray diffraction (XRD) pattern of the precipitates before calcination (not shown) display the characteristic peaks of the ZnO and small peaks which are attributed to  $(Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O)$ .

After calcination of the precipitate, the XRD patterns of the calcinated samples showed that ZnO nanoparticles with high purity were obtained. The XRD pattern of samples 100-1, 125-1, 150-1 and the ZnO estandar is shown in Figure 3. Atomic absorption analysis (Table 1) indicates that the purity of the nanoparticles is around 98%.



Figure 3. X-ray diffraction pattern of samples 100-1, 125-1, 150-1 after calcination, the standard X-ray diffraction pattern from the literature [23] is included .

Smaller particles were obtained when decreasing the addition rate of the NaOH solution, which can be explained by the smaller amount of primary nanoparticles formed at a given time, which causes a lower probability for particle coalescence and agglomeration by inter-particle collision

# Conclusions

Nanoparticles of ZnO with average particle size from 6.0 to 22 nm with high, high yield and high purity were obtained.

By decreasing the addition rate of the NaOH solution, smaller particles were produced.

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# A THEORETICAL STUDY BY MOLECULAR COUPLING (DOCKING) OF THE MECHANISM OF ENZYMATIC RING OPENING POLYMERIZATION OF LACTONES

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#### Abstract

Enzymatic ring-opening polymerization of lactones ( $\varepsilon$ -caprolactone ( $\varepsilon$ -CL),  $\delta$ -decanolactone ( $\delta$ -DL) and  $\beta$ -butyrolactone ( $\beta$ -BL)) was carried out in toluene by immobilized *Yarrowia lipolytica* lipase (YLL) and using isosorbide as initiator.

In order to explain the experimental differences in reaction times and the molecular weights and understand the activation of lactones mechanism, a theoretical study of the intermolecular interactions between the monomers and the enzyme using an *in silico* molecular couplings (molecular docking) was undertaken. By this method, the preferred binding site of the enzyme monomers and their mode of action can be determined. From these results, an explanation for the relative activity toward the different substrates used in this type of polymerization is formulated.

## Introduction

Biodegradable polymers have been attracted the interest of many researchers because of their applications in different areas related with medicine and biology. Among biodegradable materials, biodegradable polyesters have been one of the most studied, including those from the polymerization of lactones, which are cyclic esters [1]. Polymerization of lactones is generally carried out by a ring-opening polymerization mechanism using different catalysts and initiators.

Lipase chemistry has been extensively used in the synthesis of different organic and polymeric materials [2]. Interest in lipases has greatly increased in recent years, mainly due to the versatility displayed by this class of enzymes [3]. Its natural function is to hydrolyze the ester group present in the triglycerides. However, they can also participate in a wide range of synthetic reactions where different unnatural substrates are involved. The catalytic triad of lipase consists invariably of a serine, a histidine, and aspartic / glutamic acid. Based on a multiple sequence alignment, we have identified the catalytic triad residues as serine 162, aspartate 230 and histidine 289.

Methodology for Molecular Links (Molecular Doking) is a computational technique that determines how a substrate or ligand would be attached to a biomolecule active site. This includes finding the preferred substrate orientation and conformational geometry, and the calculation of the binding energy, free energy, or any other numerical measurement that estimates the degree of coupling between ligand molecules and active sites of a biological target. One of the most important outcomes obtained from docking calculations is the binding energy resulted from the interaction between the substrate and the active site. This value has been used to determine potential inhibitor capabilities of different substrates toward the enzyme action [4]. Although molecular docking can be employed to investigate the mechanism of enzyme action during a biocatalytic process, few have been done in this area of investigation [5]. In this paper, molecular

docking is employed to give insight on the mechanism of ring opening operating during enzymatic polymerization.

# Experimental

Polymers were obtained from  $\varepsilon$ -caprolactone ( $\varepsilon$ -CL),  $\delta$ -decanolactone ( $\delta$ -DL) and  $\beta$ -butyrolactone using a relationship lactone/isosorbide of 10:1 in toluene in the presence of 12 mg of immobilized lipase on macroporous resin Lewatit 1026 [2]. Reaction temperatures were in the range of 70 °C to 120 °C. For the theoretical study, crystal structure of *Yarrowia lipolytica* lipase reported and obtained by F. Bordes et al. [6] and downloaded from the Protein Data Bank [6] (PDB code 300D) was used. A resolution of 1.7 Å is reported. From the seven units, only that containing the catalytic triad (subunit A) was used for the calculations.

The structures of the monomers were built by means of the program Spartan 08 [4]. Geometry optimization was performed without symmetry constraints by quantum mechanical calculations at semiempirical PM3 level of theory and numerical accuracy with minimum base. For viewing, handling, preparation and docking study of lipase monomers, Virtual Docker Molegro for Windows software version 2010.4.2 MVD [5] was employed. Imported structure was corrected from structural errors. Once prepared, the target enzyme, a docking "blind" study was made in order to search and explore the molecular region preferred by substrates for coupling to the enzyme. The next step was to search for cavities in the enzyme: this allowed the finding of a cavity with a volume enough to host the monomer molecule. However, in the detected cavity weren't found aminoacid groups associated with the catalytic triad, so we proceeded to carry out the coupling of the monomers directly in the triad region. We evaluated the energies of the different links and the efficiency of the ligand formation, mathematically defined as the ratio of total energy coupling to the number of heavy atoms in the monomers. These values are considered as a measure of the affinity of the monomers to lipase.

# **Results and Discussion**

Yields obtained in toluene were lower than 10%, with conversions lower than 20%. Better results were obtained in the absence of solvent. In the presence of toluene, the closed configuration of the lipase is favored, as open configuration requires a polar media. This means that in a non-polar environment the catalytic triad is hidden and propagation step is inhibited.

In Table I, results obtained for bulk polymerization are depicted. Higher conversions are observed for  $\varepsilon$ -caprolactone, followed by  $\delta$ -decanolactone and  $\beta$ -butyrolactone. Reaction rates are related with the inverse of ligand efficiency (see Table II). Based on this relationship, it is clear that enzyme-lactone complex is faster for  $\varepsilon$ -caprolactone, and this fact inhibit the formation of the product, and conversion rates are slower.

The first results obtained from the Blind Docking Obtained indicated that the lactones prefer to bind to a larger cavity different from the catalytic triad, and this is mainly due to the fact that triad is hidden by the lid. In the first trial, a crystal form in the closed form was used as starting point. By this, the program does not consider the interaction between the lactone and the catalytic triad. Interactions present in this structure are mainly of hydrophobic type.

Monomer	Time (h)	Conversion (%)	Molecular Weight	Reaction Temperature
			(g/mol)	°C
ε-Caprolactone	84	88.5	1033.73	70
-	84	100	863.72	80
	84	100	1028.29	90
	84	100	1103.99	100
	12	100	1142.93	120
δ-Decanolactone	84	80.83	1750.15	70
	84	72.40	1991.96	80
	84	72.91	931.65	90
	84	82.64	2389.26	100
	12	86.70	1834.456	120
<b>β-Butyrolactone</b>	84	37.24	772.318	70
	84	53.11	1716.68	80
	84	46.66	1634.38	90
	84	41.253	1108.64	100
	12	53.40	1716.678	120

Table I. Results for the enzymatic ring opening polymerization of lactones without solvent.

Based on the accepted mechanism for lipase action, simulation was focused to the enzyme active site without the presence of the lid steric hindrance. Using this approach, interaction energies are slightly lower than those observed in the larger volume cavity were recorded.

Interactions present in the between lactones and aminoacid residues in the catalytic triad lead to the conclusion that several hydrogen bonding are being formed. Stronger hydrogen bonds are observed between serine 162 residue and the lactone (see Table II)

The map of hydrophilic and hydrophobic interactions indicates that they are mostly of hydrophobic and hydrophilic nature and not very strong, Electrostatic interactions map shows that the lactones are also found in the electron-rich area.

Monomer	efficiency of ligand	Interaction Waste	Hydrogen bond energy (Kcal)
β-Butyrolactone	9.2979	Glicine 87	-0.837536
		Serine 162	-0.946231
		Serine 162	-1.77581
		Leucine 163	-2.00693
δ-Decanolactone	6.7173	Glicine 87	-1.79898
		Serine 162	-2.5
		Leucine 163	-2.5
		Glicine 164	-1.10701
ε-Caprolactone	6.5521	Serine 162	-1.17507
_		Serine 162	-2.5
		Leucine 163	-2.48136

Table II. Condensate waste and interactions of the monomers

## Conclusions

Mechanistic studies of enzymatic polymerization by ring opening of lactones were made using Docking methodology. The lid plays an important role in the catalytic activity of the enzyme, as it regulates the exposure of the catalytic triad of the active site. Besides catalytic triad, it was found that other sites have affinity with the lactone monomers. Results at this level of calculation were linked to the observed reaction rates.

## Acknowledgements

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# Determination of the Kinetic Parameters in the Anionic Polymerization of Isoprene using n-Butyl lithium and N,N,N',N'-Tetramethylethylenediamine Considering Different Reactivities of the Structural Units

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# Abstract

A model for the anionic polymerization of isoprene using n-butyl lithium (n-BuLi) as initiator and TMEDA as microstructure modifier, considering a scheme of reaction that considers that the active sites are different in configuration was proposed. Experimental data from literature, conversion and structural units were taken. Because 1,4-cis structural units are complicated to obtain directly, we obtained these from reports of indirect measurement based on natural polyisoprene, in addition we varied the cis structural unit fraction of 0.1 to 0.9 of cis+trans to calculate the kinetic parameters using nonlinear regression. From the proposed scheme of reaction the expression of consumption rate of monomer, the formation rate of the microstructure and dyads were obtained. In addition, by means of the use of Markov chains the mathematical model was complemented to obtaining the expressions that allow estimation of the active sites fraction and the distribution of dyads, base on the conditional probabilities. The kinetic model correctly fits to the data of conversion, microstructure and dyads distribution reported in literature for the anionic polymerization with and without TMEDA.

# Introduction

The kinetic studies on the anionic polymerization of isoprene has been considered usually just one type of active site [1,2], mainly because of the experimental difficulty in distinguishing the active site that belongs to each of the isomers formed; although is generally well known that the active sites are present in multiple associated states and that it depends on the solvent, initiator level, temperature and active center modifiers. On the other hand, the microstructure determination of polyisoprene only has been accomplished with experimental analysis, principally since the experimental difficulty on distinguishing the active site that belongs to each of the isomers formed conversely; there have not been any reported studies about the possibility to obtain the microstructure and dyads distribution of polyisoprene using a kinetic scheme.

In the present work, a kinetic approximation, considering the interaction between an initiator molecule or a living polymer, with different active sites, such as cis, trans, isopropenyl and vinyl, which has its own reactivity independent of the polymer chain length, was proposed to allow modeling of the polymerization rate and sequence distribution of anionic living polymerization of isoprene with *n*-butyl lithium and N,N,N',N'-tetramethylethylenediamine (TMEDA) as active center modifier.

# **Kinetic Model Description**

The main characteristic of the kinetic model is that it takes into account the interaction between the different isoprene active sites with an initiator molecule or one living polymer, producing a geometric active site in cis, trans, isopropenyl, and vinyl configuration, which has its own reactivity independent of the polymer chain length, without termination and chain transfer reactions.



The degree of association of the active sites of the polyisoprene is of four [2]. It was considered that all the species are dissociated for a relation [n-BuLi]/[TMEDA] = 4 or greater to it [2]. The propagation rates control the polymerization process. The rate of isoprene consumption refers only to the propagation reactions, and it is expressed as:

$$-\frac{d[M]}{dt} = ((k_{CC} + k_{CT} + k_{CD} + k_{CV})[I_C] + (k_{TC} + k_{TT} + k_{TD} + k_{TV})[I_T] + (k_{DC} + k_{DT} + k_{DD} + k_{DV})[I_D] + (k_{VC} + k_{VT} + k_{VD} + k_{VV})[I_V])[M]$$

where  $[I_C]$ ,  $[I_T]$ ,  $[I_D]$  and  $[I_V]$  are the concentrations of the active sites. The rates of dyads formation are expressed by:

$$\frac{d[F_{CC}]}{dt} = k_{CC}[I_C][M] \quad \frac{d[F_{CT}]}{dt} = k_{CT}[I_C][M] \quad \frac{d[F_{CD}]}{dt} = k_{CD}[I_C][M] \quad \frac{d[F_{CV}]}{dt} = k_{CV}[I_C][M]$$
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$$\frac{d[F_{TC}]}{dt} = k_{TC}[I_T][M] \quad \frac{d[F_{TT}]}{dt} = k_{TT}[I_T][M] \quad \frac{d[F_{TD}]}{dt} = k_{TD}[I_T][M] \quad \frac{d[F_{TV}]}{dt} = k_{TV}[I_T][M]$$

$$\frac{d[F_{DC}]}{dt} = k_{DC}[I_D][M] \quad \frac{d[F_{DT}]}{dt} = k_{DT}[I_D][M] \quad \frac{d[F_{DD}]}{dt} = k_{DD}[I_D][M] \quad \frac{d[F_{DV}]}{dt} = k_{DV}[I_D][M]$$

$$\frac{d[F_{VC}]}{dt} = k_{VC}[I_V][M] \quad \frac{d[F_{VT}]}{dt} = k_{VT}[I_V][M] \quad \frac{d[F_{VD}]}{dt} = k_{VD}[I_V][M] \quad \frac{d[F_{VV}]}{dt} = k_{VV}[I_V][M]$$

Where  $F_{ij}$  represents the total quantity of the ij dyad.

The relation between the fraction of active sites and the conditional probabilities is:

$$\frac{W_{C}}{W_{T}} = \frac{(P_{TT} - 1)[(P_{DD} - 1)(P_{VV} - 1) - P_{VD}P_{DV}] - P_{DT}[P_{TD}(P_{VV} - 1) - P_{VD}P_{TV}] + P_{VT}[P_{TD}P_{DV} - P_{TV}(P_{DD} - 1)]}{-P_{CT}[(P_{DD} - 1)(P_{VV} - 1) - P_{VD}P_{DV}] + P_{DT}[P_{CD}(P_{VV} - 1) - P_{VD}P_{CV}] - P_{VT}[P_{CD}P_{DV} - (P_{DD} - 1)P_{CV}]}$$

$$\frac{W_{D}}{W_{T}} = \frac{P_{CT}[P_{TD}(P_{VV} - 1) - PV_{VD}P_{TV}] - (P_{TT} - 1)[P_{CD}(P_{VV} - 1) - P_{VD}P_{CV}] + P_{VT}[P_{CD}P_{TV} - P_{TD}P_{CV}]}{-P_{CT}[(P_{DD} - 1)(P_{VV} - 1) - P_{VD}P_{DV}] + P_{DT}[P_{CD}(P_{VV} - 1) - P_{VD}P_{CV}] - P_{VT}[P_{CD}P_{TV} - P_{TD}P_{CV}]}$$

$$\frac{W_{V}}{W_{T}} = \frac{-P_{CT}[(P_{TD}P_{DV} - (P_{DD} - 1)P_{TV}] + (P_{TT} - 1)[P_{CD}P_{TV} - (P_{DD} - 1)P_{CV}] - P_{DT}[P_{CD}P_{TV} - P_{TV}P_{CV}]}{-P_{CT}[(P_{DD} - 1)(P_{VV} - 1) - P_{VD}P_{DV}] + P_{DT}[P_{CD}(P_{VV} - 1) - P_{VD}P_{CV}] - P_{VT}[P_{CD}P_{TV} - P_{TV}P_{CV}]}$$

Pij are the conditional probabilities

#### **Procedure calculation**

The program was fed with initial data of isoprene concentration  $[M]_o$  and initiator concentration  $[I]_o$ , and with experimental data of isoprene conversion, microstructure and Bernoulli dyads. The conversion data were obtained from the kinetic equations proposed by Chang et al. [2] using temperatures of 40, 50, 60, 70 and 80 °C, with a molar ratio [TMEDA]/[I]<sub>o</sub> of 0 and 4. The initial conditions were:

$$[P_x] = 0, \qquad x = 2, 3, 4, \cdots$$
$$[I_C] = W_C[I]_o$$
$$[I_T] = W_T[I]_o$$
$$[I_D] = W_D[I]_o$$

Dyads were calculated considering a random distribution (Bernoulli) [3] from the values of reported microstructure [4]. In addition, it was considered that the microstructure does not change with the monomer conversion [5], and because 1,4-cis structural units are complicated to obtain directly, we obtained these from reports of indirect measurement based on natural polyisoprene [4,5], in addition we varied the cis structural units fraction of 0.10 to 0.90 with R = cis/(cis+trans). For the polymerization conditions does not be vinyl units [4,5]. The estimation of the rate constants was realized using the nonlinear multivariate regression method, which considers the error of all the variables [6].

#### **Results and discussion**

The table 1 shows the experimental and calculated sequence distribution. The kinetic model suitably predicts the sequence distribution and microstructure. With respect to the microstructure, the error is < 2.0 %, i.e., the differences between the experimental and calculated data does not exist practically. For the dyad distribution, the calculated and experimental data are similar, with an error least that 2 %. In general terms, the values predicted by the kinetic model are acceptable. The Figure 1 shows the adjustment isoprene conversion.

It can be observed that the obtained activation energies are: to nonmodified system 70.615 kJ/mol, and to the modified system 43.219 kJ/mol. These values are similar reported by Halasa et al. [2]. It can be mentioned that by considering the same active site, the polymerization reaction for this system can occur, owing to the steric factors. This is observed with activation energy and activation entropy.

MR = 0	CC	СТ	CD	TC	TT	TD	DC	DT	DD
exp	6.0856	14.1997	4.3837	14.1997	33.1327	10.2286	10.2286 4.3837		3.1577
calc	6.0921	14.2533	4.3797	14.1468	33.0986	10.2727	4.3751	10.2362	3.1454
error(%)	0.1067	0.3776	0.0898	0.3725	0.1029	0.4313	0.1956	0.0745	0.3914
MR = 4	CC	СТ	CD	TC	TT	TD	DC	DT	DD
exp	2.2907	5.3449	7.4994	5.3449	12.4715	17.4986	7.4994	17.4986	24.5520
calc	2.2772	5.3279	7.4854	5.3279	12.4653	17.5131	7.4854	17.5131	24.6050
error(%)	0.5884	0.3195	0.1872	0.3195	0.0497	0.0828	0.1872	0.0828	0.2156

**Table 1.** Sequence distribution of the polymerization of isoprene isoprene at different relation MR ( $[TMEDA]/[n-BuLi]_0$ ) and R = 0.30

## Conclusions

A kinetic model that considers four geometric active sites cis, trans, isopropenyl and vinyl was proposed to study the polymerization reaction of isoprene prepared by means of anionic living polymerization using an initiator composed of *n*-butyl lithium and tetramethylethylenediamine as modifier. The system components determined the reactivity of the active sites, with each of them having a different capacity to add a new isoprene molecule in any of the isomeric forms. The model was able to reproduce the conversion data and dyad distribution with relatively small errors. The sequence distribution was determined from the beginning of the reaction, which defined the

properties of the polymer. As the reaction advanced, only the molecular weight of the isomeric chain increased. The kinetic model was in agreement with the experimental data, and also provided the reactivity of each active site and allowed obtaining the sequence distribution.



Figure 1. Isoprene conversion as function of polymerization time at MR = 0 and 4, at 50, 60, 70 and 80 °C.

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## A KINETIC STUDY OF THE RING-OPENING POLYMERIZATION OF EPSILON-CAPROLACTONE INITIATED BY MOLYBDENUM TRIOXIDE

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PCL and its copolymers can be obtained by several different procedures. The widely used route for the preparation of high molecular weight polymers is ring-opening polymerization (ROP) of  $\varepsilon$ -CL catalyzed by different organometallic or metallic catalysts, such as tetraphenylthin, stannous chloride and stannous octoate [1,2]. We have reported the synthesis of polyesters and copolyesteres by ring-opening polymerization using catalysis with molybdenum derivatives [3-5]. Catalysis by molybdenum derivatives proceeds by heterogeneous catalysis. One of the main advantages of heterogeneous catalysis is their potential of separation and recycling for repeated usage in a reaction.

In this investigation, a kinetic study of the ring-opening polymerization of epsilon-caprolactone catalyzed by molybdenum trioxide MoO3 at 150°C was undertaken. Effect of hydroxylic co-initiators (water, alcohols) was determined. Plots of degree of conversion (obtained by 1H-NMR) against time were fitted to different kinetic models. The scope of this mathematical analysis on the polymerization mechanism will be discussed.

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# STUDY OF FREE BORDER EFFECT IN GLASS FIBRE REINFORCED MULTIAXIAL STRUCTURAL LAMINATES

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#### Abstract

In multirectional laminates that exhibit free arista, a free border effect can be appreciated. It consists of the presence of important interlaminar stresses that can generate failure by delamination. The appearance of the free border phenomena does not require the presence of off-plane loads, but they are produced simply under uniaxial load state (traction or compression). In this research, a detailed study was carried out by analyzing de effect of the tridimensional structure of type E glass fiber based textiles on the stress component to the off-plane direction in the border of a laminate (border effect). Laminates were manufactured by embedding six mutiaxial textile layers into an epoxy resin matrix. Such textiles posses a tridimensional structure with staking sequence of  $[0^{\circ}/+45^{\circ}/90^{\circ}/-45^{\circ}]$ . The unidirectional fiber bundles in the four layers are held together by a fine polyester thread in both sides. In the outer layer where fibers are running at 0°, the polyester (PES) thread is knitted in a zig-zag pattern whereas, in the other side (outer layer at -45°), it is knitted at 0° direction. The border effect in the stress distribution and the perturbation in the strain field were evaluated in the laminates. The concept of extensometric roseta gauge was used to determine tress and shear strains in the laminate border.

#### Introduction

In the last decade have seen great attention to textile fabric reinforced composites. Composites made from woven and braided fabric reinforcements have found potential applications in the aerospace, automobile, and marine industries. This is because they have better out of plane stiffness, strength, and toughness properties, lower fabrication costs and easier handling in production quality than tape laminates. Characterization of these textile fabric composites is essential for structural design. As a consequence of the complex architectures of the textile fabrics, many parameters influence the mechanical performance of fabric composites. Many earlier research works based on the hybrid system have been reported in the literature [1-5]. The potential advantages of combining two kinds of fiber in a common resin matrix have been discussed in several recent papers [5-8]. Many investigations have focused on the influence of either chemical or environmental effects on the various composite system properties [9–12]. The increased use of laminated polymer textile composites also requires the understanding of the fracture behavior in the translayer or translaminar modes. Several researchers have paint attention to understand the failure mechanism in textile composites [13-18]. Masters & Ifju [13] conducted an experimental program to define the mechanical response of three two-dimensional triaxially braided textile composite materials to tensile loading. Moire's interferometry was used to define the full field strain distributions on the surface of the specimens and enhanced X-ray to identify the damage mechanisms was also used. Ivanov et al. [14] described damage and failure behaviour of triaxial braided carbon/epoxy composites under tension. The tensile tests were instrumented with optical surface strain and acoustic emission measurements. On the other hands, Karkkainen and Sankar [15] analyzed a textile composite from a micromechanical point of view assumed that the stress state is not uniform across the representative volume element. By means of finite element models,

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Ernst et al. [16] showed that the translaminar fracture is a combination of tensile and bending loads. The delamination can cause significant reduction of structural integrity, especially in terms of strength and stiffness, which often leads to catastrophic failure without much warning in advance. In multirectional laminates that exhibit free arista, a free border effect can be appreciated. It consists of the presence of important interlaminar stresses that can generate failure by delamination. The appearance of the free border phenomena does not require the presence of off-plane loads, but they are produced simply under uniaxial load state (traction or compression). In this paper, a study was carried out by analyzing de effect of the tridimensional structure of type E glass fiber based textiles on the stress component to the off-plane direction in the border of a laminate (border effect) and the mechanics associated with these complex fiber architectures.

## Experimental

The material that was studied in this research was a glass-fiber non-crimp fabric reinforced epoxy composite. The multi-axial E-glass reinforcement textile (provided by Italian industry Nastrificio Gavazzi) has a mass per unit area of  $972 \pm 5\%$  g/m2 and a [0°, +45°, 90°, -45°] stacking sequence. The layers have relative mass fractions and are stitched together with a polyester (PES) multifil binding yarn. A Diglycidyl ether of Bisphenol A (DGEBA) based epoxy resin, (Epon 828 from Shell Chemical Company) was used as matrix and Metaphenilene diamine (mPDA) ACS reagent grade was used as a curing agent. The multiaxial textile ( $0^\circ$ ,  $\pm 45^\circ$ ,  $90^\circ$ ) composites laminates were manufactured by wet lay-up process. A six stacking sequence were impregnated with epoxy-MPDA mixture (the curing agent concentration was 14.5 parts by weight per hundred parts of the epoxy resin). Then, the assembly was transferred to an oven to curing cycle (Squaroid, Model 3608-5, for 2 h at 75 °C and 2 h at 125 °C) until the curing cycle was completed. After this time, the lamina was cooled down to room temperature and finally it was withdrawn from the oven to get the samples for mechanical test. The specimens were cut to size of 229 mm  $\times$  13.0 mm  $\times$  2.0 mm with major length in the fiber direction from unidirectional composite laminate panel using a high speed diamond bench cutter according to ASTM standard D3039-76. A Shimadzu universal machine was used to carry out mechanical tests with crosshead speed of 2.0 mm/min.

Classical Lamination Theory. Elasticity Formulation.

It is necessary to calculate the out-of-plane stress at the specimen edges to evaluate edge delamination. Thus, 3D stress analysis was carried out using a finite difference approach. The model applied in this analysis is that of a cross-ply laminate of the form  $(0^\circ, \pm 45^\circ, 90^\circ)$ . The stress-strain relation considered by Pipes and Pagano [19] was used and is shown in Eq. 1. The stress-strain relations for each orthotropic layer in principal material directions are:

$$\begin{bmatrix} \sigma_{1} \\ \sigma_{2} \\ \sigma_{3} \\ \tau_{23} \\ \tau_{31} \\ \tau_{12} \end{bmatrix} = \begin{bmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ C_{12} & C_{22} & C_{23} & 0 & 0 & 0 \\ C_{13} & C_{23} & C_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{55} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{66} \end{bmatrix} \begin{bmatrix} \varepsilon_{1} \\ \varepsilon_{2} \\ \varepsilon_{3} \\ \gamma_{23} \\ \gamma_{31} \\ \gamma_{12} \end{bmatrix}$$
(1)

and can, upon transformation of coordinates in the 1-2 plane, be expressed in laminate coordinates as

$$\begin{bmatrix} \sigma_{x} \\ \sigma_{y} \\ \sigma_{z} \\ \tau_{yz} \\ \tau_{zx} \\ \tau_{xy} \end{bmatrix} = \begin{bmatrix} \overline{C}_{11} & \overline{C}_{12} & \overline{C}_{13} & 0 & 0 & \overline{C}_{16} \\ \overline{C}_{12} & \overline{C}_{22} & \overline{C}_{23} & 0 & 0 & \overline{C}_{26} \\ \overline{C}_{13} & \overline{C}_{23} & \overline{C}_{33} & 0 & 0 & \overline{C}_{36} \\ 0 & 0 & 0 & \overline{C}_{44} & \overline{C}_{45} & 0 \\ 0 & 0 & 0 & \overline{C}_{45} & \overline{C}_{55} & 0 \\ \overline{C}_{16} & \overline{C}_{26} & \overline{C}_{36} & 0 & 0 & \overline{C}_{66} \end{bmatrix} \begin{bmatrix} \varepsilon_{x} \\ \varepsilon_{y} \\ \varepsilon_{z} \\ \gamma_{yz} \\ \gamma_{zx} \\ \gamma_{xy} \end{bmatrix}$$
(2)

The strain-displacement relations are

$$\varepsilon_{x} = u_{,x} \quad \varepsilon_{y} = V_{,y} \quad \varepsilon_{z} = W_{,z}$$

$$\gamma_{yz} = V_{,z} + W_{,y} \quad \gamma_{zx} = W_{,x} + u_{,z} \quad \gamma_{xy} = u_{,y} + V_{,x}$$
(3)

where a comma denotes partial differentiation of the principal symbol with respect to the subscript.

If the laminate is subjected to uniform axial extension on the ends x = constant, then all stresses are independent of x. The stress-displacement relations are obtained by substituting the straindisplacement relations, Equation (3), in the stress-strain relations, Equation (2). Next, the stressdisplacement relations can be integrated under the condition that all stresses are functions of y and z only to obtain, after imposing symmetry and antisymmetry conditions, the form of the displacement field for the present problem:

$$u = kx + U(y, z) \quad v = V(y, z) \quad w = W(y, z)$$

$$(4)$$

The stress-equilibrium equations then reduce to

$$\tau_{xy,y} + \tau_{zx,z} = 0$$

$$\sigma_{y,y} + \tau_{yz,z} = 0$$

$$\tau_{yz,z} + \sigma_{z,z} = 0$$
(5)

Upon substitution of the displacement field, Equation (4), in the stress-displacement relations and subsequently in the stress-equilibrium differential equations, Equation (5), the displacement equilibrium equations are, for each layer,

$$\overline{C}_{66}U_{,yy} + \overline{C}_{55}U_{,zz} + \overline{C}_{26}V_{,yy} + \overline{C}_{45}V_{,zz} + (\overline{C}_{36} + \overline{C}_{45})W_{,yz} = 0$$

$$\overline{C}_{26}U_{,yy} + \overline{C}_{45}U_{,zz} + \overline{C}_{22}V_{,yy} + \overline{C}_{44}V_{,zz} + (\overline{C}_{23} + \overline{C}_{44})W_{,yz} = 0$$

$$(\overline{C}_{45} + \overline{C}_{36})U_{,yz} + (\overline{C}_{44} + \overline{C}_{23})V_{,yz} + \overline{C}_{44}W_{,yy} + \overline{C}_{33}W_{,zz} = 0$$
(6)

These coupled second-order partial differential equations do not have a closed-form solution. Accordingly, the approximate numerical technique of finite differences is employed. First, however, the boundary conditions must be prescribed in order to complete the formulation of the problem. Symmetry of the laminate about several planes permits reduction of the region of consideration to a quarter of the laminate cross section in the y-z plane at any value of x as shown in Figure 1. There, along the stress-free upper surface,

$$\tau_{xz} = 0 \quad \sigma_z = 0 \quad \tau_{yz} = 0$$

along the stress-free outer edge,

$$\tau_{xy} = 0 \quad \sigma_{y} = 0 \quad \tau_{yz} = 0 \tag{8}$$

along the middle surface, Z = 0, because U and V must be symmetric and W antisymmetric,

$$U_{z}(y,0)=0 \quad V_{z}(y,0)=0 \quad W(y,0)=0$$
(9)  
and along the line y = 0, because U and V must be antisymmetric and W symmetric,  
$$U(0,z)=0 \quad V(0,z)=0 \quad W_{y}(0,z)=0$$
(10)



Figure 1. Finite difference representation and boundary conditions [19].

At the corner (b, 2ho) of the region, five stress conditions apparently govern the behavior. However, the problem would be over specified if all five conditions were imposed at the same time. Rather, three are specified and, subsequently, the remaining two are seen to be automatically satisfied thereby acting as a built-in verification of the numerical results. Numerical experimentation revealed that the choice of the three conditions is immaterial; the remaining two are always satisfied. The numerical solution was obtained by the finite difference method. The two regions (layers) indicated in Figure 1 are represented with a series of regularly spaced material points as shown. At each point, the differential equations are approximated by finite difference operators (central difference operators inside the region with forward and backward difference operators being used at the boundaries). At the interface between layers, the continuity conditions for U, V, W,  $\sigma$  z,  $\tau$ xz, and  $\tau$ yz are approximately satisfied by locating material points symmetrically about the interface. The resulting finite difference equations constitute a set of nonhomogeneous linear algebraic equations. Because there are three dependent variables, the number of equations in the set is three times the number of material points.

#### **Results and Discussion**

The figure 2 shows the distributions of the stresses  $\sigma x$ ,  $\tau yx$  and  $\tau yz$  at the interface between layers. There, the stresses predicted with classical lamination theory are obtained in the central portion of the cross section. However, as the free edge is approached,  $\sigma x$  decreases,  $\tau yx$  goes to zero, and, most significantly,  $\tau yz$  increases from zero to Infinity. By use of other laminate geometries, the width of the region in which the stresses differ from those of classical lamination theory has been shown to be about the thickness of the laminate, 4ho. Thus, the deviation from

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classical lamination theory can be regarded as a boundary layer or edge effect. One laminate thickness away from the edge, classical lamination theory is expected to be valid.



Longitudinal Young's modulus	EL	GPa	32.0
Transverse Young's modulus	ET	GPa	32.0
In-plane shear modulus	GLT	GPa	3.4
Out-of-plane shear modulus	GTT	GPa	2.3
In-plane Poisson's ratio	ΠLT		0.2
Out-of-plane Poisson's ratio	ШΤТ		0.4

Figure 2. Stresses at the interface.

The figure 3 presents the damage development in the samples subjected to tensile load. The existence of interlaminar stress near free edges is evident.





Figure 3. Damage development on the edge of the composite laminate.

In order to figure out failure mechanism produced textile composite laminate a finite element model was computed and the results are shown in figure 4. The axial displacements determined by finite element analysis are shown along with the elasticity solution. If an orthotropic lamina is loaded off-axis with a tensile stress, then shear-extension coupling exists, leading to an originally rectangular shape both elongating and shearing into a parallelogram. That shape is the natural shape toward which even a lamina in a laminate is tending as we observe the behavior as we go away from the interface between the two top layers ( $\pm \alpha$ . layers that must be a rectangle at their interface). Thus, a line drawn horizontally across the specimen in Figure 4 before loading tends to deform into a diagonal line indicating shear deformation. However, the influence in the top layer of the shear stress  $\tau xz$ , which is high at the free edge and quickly decreases in the direction away from the edge and in the direction toward the top surface, is to deform the diagonal line more at the free edge than as the middle of the laminate is approached. Thus, the predicted surface deformation is the somewhat S-shaped divergence from a straight line. That predicted divergence is plotted with the measured deformation in Figure 2 where we see excellent agreement. Thus, the physical existence of interlaminar stresses has been clearly demonstrated. This founding are in agreement with Pipes and Daniel [20].



Figure 4. Finite element method modeling for tensile load in textile composite laminates.

In flexural test the crack initiation was observed in the free edge such as is observed in figure 4. that figure shows interlaminar stress distributions in the in-plane direction at the 45/-45 interface of [45/-45]s laminates. Interlaminar stresses converge well as the iteration continues. Figure 5 shows interlaminar stress distribution in the in-plane direction at the 0/90 interface of [45/-45/0/90]s laminates. The peak stress increases as the iteration continues. They show that peak stresses occur at the interfaces.



Figure 5. Flexural test samples.

## Conclusions

In this paper, the stress analysis of  $(0^\circ, \pm 45^\circ, 90^\circ)$  laminates was conducted considering the freeedge effect. The main conclusions obtained are:

An extended formulation for interlaminar stress analysis for unsymmetric laminates is introduced. Classical assumptions have been justified, new approximations have been established, a number of cases of stacking and loading have been checked and compared to the symmetric case.

The edge effect is more dominant in tension loading than in bending for both symmetric and unsymmetric angle-ply laminates.

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## XPS STUDY OF ORGANOMETALLIC COMPOUNDS OF TITANIUM AND CARBON OXIDES FORMED BY GLOW DISCHARGES

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This work presents a study about the structure of organometallic matrices of titanium and carbon oxides formed with tetra titanium propoxide (TTP) oxidized with rf resistive glow discharges of water. These materials are being studied as part of photosensitive semiconductor polymeric membranes for solar cells. TTP has 4 chains of hydrocarbons (3C) that rearrange due to collisions of electrons and ions accelerated in an electric field to produce partial separation of organic and metallic segments of TTP. This forms plain and spherical matrices of titanium and hydrocarbon oxides as a function of the energy applied in the synthesis. The XPS study presented in this work is aimed to establish the main chemical states of Ti, C and O. The narrow scans involve binding energy related to -C-Ti, -C-, -C-O- and O-C=O (bonds not showed in C belong to H). Oxygen showed a complex energy distribution with metallic (Ti) and organic (C) oxides. On its part, Ti showed Ti<sup>4+</sup> for 2p3/2 and 2p<sup>1</sup>/<sub>2</sub> orbitals.

# STUDY OF QUARRY STONE PERMEABILITY MODIFICATION BY HEXAMETHYLDISILOXANE PLASMA POLYMERIZATION AT LOW AND ATMOSPHERIC PRESSURE

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#### Abstract

This work shows the results of the high hydrophobicity of quarry stone covered with a film of polihexametildisiloxane (PPHMDSO) synthesized by atmospheric plasma discharge with 30min of reaction time. The absorption of water in the stone quarry is discussed. The contact angles found, clearly shows the high hydrophobicity 125°. The FT-IR spectra have the characteristic functional groups such as CH<sub>3</sub>, Si-CH<sub>3</sub>. This clearly favors the high hydrophobicity in the stone quarry.

#### Introduction

Historical buildings and monuments of art are daily subjected to deterioration by the action of physical, chemical and biological agents. This deterioration involves changing the structural stability in the stone and the invasion of harmful microorganisms to the nature of the stone [1]. To prevent and stop these phenomena of deterioration, you can use products based on ethyl silicate in the absence of cementations matrix, set the grains of clay material, providing strength and durability. To ensure the reliability of interventions with these products, it is necessary to carry out some previous studies, in order to define the right mix of consolidating employment and select the most appropriate type for each particular case, since the reliability of these products depends largely on the microstructure of the material considered. [2]. In trying to stop the deterioration that occurs in historical monuments, the complexity lies in understanding the morphology of the stone quarry, this is made of a granular texture and a micro laminate. Either of these situations match the exposed surface of the stone outside the building, and affect their surface deterioration differently [3-7] Using HMDSO synthesized by low pressure plasma has produced excellent results, obtaining protective films which clearly show that surface modification does not change the texture or color of the substrate. The surface energy and wettability of the films was characterized using infrared spectroscopy with Fourier transform (FTIR) and contact angle measurement [8, 9].

## **Experimental**

Figure 1 shows a schematic representation of the reactor for the resistive coupling plasma discharge. The reactor has a glass tube (Pyrex) with the following dimensions, length 250 mm, internal diameter 83 mm, the thickness of the glass is 7 mm in the central part has an input area for monomer of 1 cm in diameter, this in order to ensure that what goes into the reaction chamber is ionized directly. It has stainless steel caps at the ends, these caps have access to the discharge electrodes 40 mm x 40 mm, and outlets to connect the vacuum pump and the remote sensor.

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Importantly, the electrodes are coated with a glass surface to ensure a homogeneous discharge; the distance from the discharge electrodes is 15mm. The reaction conditions were 2.4 Torr, 30 and 50 W with a frequency of 13.5 MHz plasma The substrate is white stone blocks of dimensions 40 mm x 40 mm and a thickness of 5 mm, the substrate was cleaned with acetone and was introduced into the flask for 3 h. at 100  $^{\circ}$  C. In order to evaluate the deposited film, 3 tablets of 99% KBr (Sigma-Aldrich) were also introduced into the reaction chamber, 2 mounted at the ends of the reactor and 1 in the center by the stone exposed to the plasma of hexamethyldisiloxane (HMDSO) grade 99.5% (Aldrich) in order to verify that the discharge across the reactor occurs homogeneously.



The characterization of the coating surface was done using the technique of contact angle with a camera with 30X optical zoom and 16MP, angles found in the modified stone are of 130 degrees, as is shown in Figure 2. KBr tablets were analyzed with a Perkin-Elmer 2000 FT-IR spectrophotometer with a wavelength between 4000 and 400 cm<sup>-1</sup> and 32 scans.



Figure 2.Quarry stone property / drop of water

Figure 3 shows the FT-IR spectra of the 2 tablets exposed to plasma for 30 min. You can verify that the Si-CH<sub>3</sub> functional groups are clearly marked on the characteristic bands of the methyl groups and methyl silane. It is clear that methyl silane is more abundant; this is manifested in the spectrum and the high hydrophobicity of the material. Widest vibrations are marked in 1070 that correspond to the group of silanes, can also appreciate the silane methyl functional groups in the bands 3440 and 1260, this is shown in Table 1[9,12].



Figure 3 FT-IR PPHMDSO

Table 1

Wavenumber (cm <sup>-1</sup> )	Assignment
3440	Si-CH₃
2980–2850	$CH_3, CH_2$
1260	Si–(CH <sub>3</sub> )
1200–1000	SiO <i>x</i> , Si–O–Si
900–750	CH₃

Figure 4 shows that the absorption of water in the stone quarry is small, since for a reasonably long time the stone stops absorbing water, due to the PPHMDSO coating. The graph shows an exponential behavior and the increment in the system mass is only half a gram, which indicates that coating is a very good hydrophobic layer. The graph shows that the modified stone absorbed .5 grams in the first 100 minutes of continuous exposure to water, then in the next 600 min practically no water diffuses into the stone, so clearly there is an exponential behavior.



#### Conclusions

The stone quarry modified by atmospheric plasma has high hydrophobicity hexamethyldisiloxane, this is shown in FT-IR spectrum. Download times are even lower than those used in low pressure plasma, the spectra of FT-IR and let it show. It works in the electronic device that generates shocks of 5-12 kV.

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# TITANIUM OXIDE AND POLYETHYLENE MATRICES FORMED BY PLASMAS OF TITANIUM ISOPROPOXIDE

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This work presents a study about the synthesis by plasma of organometallic compounds of titanium oxides obtained from titanium isopropoxide (TTIP) and water on polyethylene (PE). The objective is to form titanium oxide particles supported on PE matrixes for use in fotoassisted degradation of pollutants. This kind of supports is needed to fix small particles, in the order of nano and meso dimensions, apart from streams of effluents.

TTIP is an organometallic compound formed by a central Ti atom surrounded by 4 O atoms, which in turn are linked by chains of 3 C. The role of the accelerated particles in the plasma is to separate the organic and inorganic segments of TTIP bonding the TiO phase to PE. The synthesis was carried out by plasma in a tubular glass reactor of 750 cm<sup>3</sup>, 9 cm to  $10^{-1}$  mbar and power between 100 and 150 W. The result was white powder formed of agglomerates of spherical organometallic particles with a diameter between 160 and 582 nm linked to PE. The agglomerates contain titanium and carbon oxides with a tendency to change from film to particles as a function of the energy applied in the synthesis.

# EFECT OF DEGREE OF NEUTRALIZATION IN THERMAL BEHAVIOR AND WATER ABSORPTION CAPACITY OF HYDROGELS BASED ON ACRYLIC ACID.

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# Abstract

Different hydrogels, based on acrylic acid, were synthesized by radical polymerization and neutralized with two different quantities of NaOH. The synthesized hydrogels were characterized by Fourier Transform Infrared Spectroscopy (FTIR), and Thermogravimetric analysis. The molecular weight was determined by viscosimetry showing that the molecular weights of the hydrogels were different. Thus monomer neutralization has an important effect, with a molecular weight decrement trend when neutralization percentage was increased. The absorption capacity was determined with distilled water and the obtained results indicate that the water absorption capacity and the thermal behavior were influenced with the extent of neutralization of the synthetic materials. The glass transition temperature was displaced and thermal resistance was affected.

# Introduction

Hydrogels are polymers in a three-dimensional network arrangement, able to retain large amounts of water. In order to keep the spatial structure, the polymer chains are usually physically or chemically crosslinked. Due to their swelling capacity, hydrogels can be easily rinsed to remove pollutant residues. The great water retention capacity makes hydrogels a special class of materials. Their network structure is the result not only of covalent bonding but also ionic, hydrogen or even Van derWaals interactions. The unique physical properties of hydrogels such as high water affinity, high thermal and mechanical stability, biocompatibility, allows a variety of industrial applications [1-3], like due to their swelling capacity, hydrogels can be easily rinsed to remove pollutant residues.

Numerous applications have been found or envisioned for these materials. Like wound dressing, controlled-release drug delivery systems, biocompatibility, water absorbents, adsorbents for metal ions and catalysis applications [4], also as polymeric gel electrolytes for electrochemical studies [5].

Modification of the hydrogels by partial neutralization has allowed them to become waterswellable polymers which have been proven to give the best performance versus cost ratio, in water they swell to a rubbery gel that in some cases can be up to 99% w/w water [6].

# Experimental

# **Polymer synthesis**

Hydrogels based on acrylic acids with different degree of neutralization, 20% of Neutralization (20% N), 40% of Neutralization (40% N) and without neutralization (0%N), were synthesized by following procedure: Acrylic Acid was dissolve in distilled water and then neutralized with NaOH solution, in a round-bottom three-neck flask equipped with stirred, a condenser and thermometer. The radical initiator and crosslinked were added in the stirring solution. After polymerization, the

resulting product was dried at 80°C for 24 hr. then washed several times with distilled water and dried again at the same conditions.

## Characterization

## **Molecular Weight**

For each sample the molecular weight was determined by intrinsic viscosimetry, using a Cannon viscometer, the solution was at 25°C. The Mark-Houwink-Sakurada equation was used to relate the intrinsic viscosity with molecular weight.

$$[\eta] = K \overline{M_v^a}$$

Where  $M_v$  is the viscosity-average molecular weight defined for a discrete distribution of molecular weights, both v and a are a empirical constants that are specific for a given polymer.

## Swelling capacity

In order to test the swelling, samples in the range weight of 0.20 to 0.40 g were used. Each sample was immersed in distilled water at room temperature for 2 hours to reach swelling equilibrium, which resulted in the absorption of water into the network of hydrogel. The sample's weight at initial (wi) and at several times (wt) was recorded to see the evolution of the swelling process. Thus, the swelling percentage (capacity) was calculated from the following equation.

$$s(\%) = \frac{w_t - w_i}{w_i} * 100$$

## **FTIR** analysis

IR spectra of the hydrogels were obtained using an spectrometer FTIR Nicolet-1700 with the ATR (Attenuated Total Reflectance) accessory, in the range of 4000-400 cm-1. The samples were not previously treated and they were just dried.

## **TGA analysis**

Thermal stability studies were performed on a Thermo-Cahn Versa Therm HS Thermogravimetric analyzer in the temperature range of 25-650°C and a heating rate of 10°C/min, using dry nitrogen for purging with a flow rate of 20 ml/min.

#### **Results and Discussion**

#### **Molecular Weight**

The degree of neutralization has a high influence on the molecular weight of the hydrogels. Molecular weight decreased as the degree of neutralization increased, this is because the NaOH is acting as a shortstop and limits the growth of polymer chains. In the following table, the obtained molecular weights are shown.

Table 1	. Molecular	weight
---------	-------------	--------

Sample	M <sub>v</sub> g/mol				
0% N	2,201				
20% N	841				
40% N	200				

## **Swelling Capacity**

The swelling capacity in distilled water of the synthesized hydrogels with different degree of neutralization is show in Fig. 1.



Fig. 1 Effect of Degree of Neutralization of hydrogels on swelling.

It is clear that the degree of neutralization plays an important role in the swelling capacity of the hydrogels. It is observed that the swelling capacity of the hydrogel 0%N is very low in comparison with both neutralized hydrogel. Regarding the neutralized hydrogels, it is observed that there is a point where 20% N begins to exceed the 40% N, this might be due to a lower mechanical resistance of the last beginning to break. The higher degree of neutralization means more carboxilate groups (-COO-) than carboxilic groups (-COOH) along the backbone. Thus, the negative charges provide repulsion of the chains allowing the diffusion of water within the polymer matrix.

## FTIR analysis

The FTIR spectra of hydrogels are shown in Fig. 2. In this Figure, the characteristics functional groups are indicated.



Fig. 2. Infrared Spectra of different hydrogels

In the three curves the absorption peeks at 2900 cm-1 is attributed to -CH2- stretching. For the spectrum of 20%N, the band at 1700 cm-1 is attributed to C=O stretching, the band at 1180 cm-1 is attributed to C-O stretching vibration, and the O-H broad band is also present between 2700 and 3400 cm-1 and between 900 and 650 cm-1 range a moderate absorption bands appears, which indicate a carboxylic acid group. When the polymer is partially neutralize, 20%N and 40%N, the C=O band is shifted to lower absorption region at 1600 cm-1 and 1400 cm-1 respectively and also their intensity is raised as the degree of neutralization is increased. Those bands can be attributed to stretching of group COO-. The O-H stretch band of carboxylic acids in the polymer without neutralization is so broad because carboxylic acids might exist as hydrogen-bonded in the polymer network. This band is shifted to higher frequencies and becomes sharper with the degree of neutralization.

#### **TGA** analysis

The TGA curves for the different synthesized hydrogel are presented in Fig. 3. It is observed that thermal resistance was modified with the neutralization degree.



Fig. 3. TGA curves of (a) PAA 0%N, (b) PAA 20%N (c) PAA 40%N.

In terms of thermal resistance, it is reduced when neutralization degree increased, for example, at 3 % of lost weight the temperature for such point was lower as the neutralization degree increased (150, 137 and 120 °C) as it can be seen in the curves a, b and c, respectively. The decomposition of sample a is in one step within a range of about 150-450 °C; samples b and c decompose in multiple steps and in a wider range, for sample b is about 137-450 °C and for sample c is 120-450°C. Residuals of the samples b and c are consistent with the percentage of neutralization.

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# SWELLING KINETICS OF HYDROGELS FROM POLI(ACID ACRYLIC/GLYCEROL DIACRYLATE-C0-SULFOPROPYL METHACRYLATE POTASSIUM SALT)

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#### Abstract

In recent years several researches have been conducted in order to create new polymeric materials with specific properties, among them are the so-called chemical gradient materials, whose promote new methods of synthesis. In this way in the present work we report the use of spherical particles of poly (acrylic acid) (PAA) hydrogels, with aqueous solutions of 3-sulfopropyl methacrylate potassium salt (SMP) and glycerol diacrylate (DGA), diffused inside them. The composition and diffusion time, were varied maintaining a constant temperature of 25 °C. The reaction system was photo polymerized using as an initiator Darocur 4265, activated with a UV lamp model VCL 7000-1, 118 volt, 15 W. The hydrogels were characterized by Raman spectroscopy. Hydrogels swelling capacity was acquired gravimetrically. It was found that materials with higher amount of glycerol diacrylate, and longer diffusion time of the co monomer solution, swelled in a lesser degree.

#### Introduction

The polymers are important materials in modern life and gels are one such type of materials. In a gel, long polymer chains are cross-linked producing a three-dimensional network, which is able to retain a liquid. In many applications this liquid is water, and the hydrophilic gels that retain big quantities of water inside their microscopic network are known as hydrogels. They can swell in water to an equilibrium volume while preserving their shape and transparency. The nature of polymeric network bonding and functional groups along the chains can be modified by the use of chemical agents, temperature, pH changes, among other factors. In general, macroscopic changes in the shape of hydrogel are reversible and produce materials that can be used as 'microscopic sponges' or systems that retain and deliver diverse chemical substances [1–3]. Polymeric hydrogels have many applications and are currently used in hygienic products, paints, food, agriculture, electronic devices, molecular filters and drug delivery systems [1, 4–9].

Photo polymerization is an alternative method to redox polymerization for the synthesis of hydrogels, which allows a better control on the kinetics of reaction, because it ensures the homogeneity of the system. We have observed that the physical structure of a hydrogels depends on the thermal history of the material. However, the chemical composition of the hydrogels creates differences in the ability of hydration of the same. For this reason in this work we propose the synthesis of hydrogels with gradient chemical composition, obtained for photo polymerization

#### Experimental

Commercial beads of poly (acrylic acid), with average size of 0.65 mm, was used as the spherical particles, meanwhile 3-sulfopropyl methacrylate potassium salt (SMP) was employed as functionalized monomer and glycerol diacrylate (DGA) as crosslinker. Other materials used are distilled water and polymerization initiator Darocur 4265.

A solution containing SMP monomer, DGA and the photo initiator solution according to Table 1, was let to diffuse into a monolayer of P(AA) beads at several temperatures, the swelling behavior as a function of time was followed by a gravimetric method. After diffusion, beads were surface dried, and immediately allocated to polymerize SMP monomer, using four UV 15 watts lamps (General Electric F10T5) rich in radiation of 350 nm wavelength, during 1 hr (to assure total conversion).

			·
	Solution A	Solution B	Solution C
Water	50 g	50 g	50 g
SMP	45 g	40 g	35 g
Glycerol diacrylate	5 g	10 g	15 g
Darocur 4265	1 mL	1 mL	1 mL

Table 1. Polymerization recipe used to prepare the poly(AA/ DGA-co-SMP) beads

To determine the swelling behavior of the hydrogels, the beads first were dried to obtain xerogels, after that were weighted and immersed in sealed glass flasks containing distilled water, until they reached maximum swelling, and then were weighted to determine their swelling capacity. Data was obtained at different time intervals after the hydrogels were immersed on water, the beads was retired from the water flask, their surface was carefully wiped to eliminate excess water and then weighted again, after that the beads was returned to the storage container. This procedure was repeated until to obtain a constant weight of the beads.

The water absorption, Sw, for the hydrogels was calculated as follows:

$$Sw = \left(\frac{m(t) - mo}{mo}\right) \tag{1}$$

Where m(t) and *mo* are the weight of the hydrogels at time *t* and the weight of the xerogels, respectively. Swelling kinetics data was correlated with two mathematical models: The first is a power law described as follows:

$$\frac{S_w}{S_\infty} = Kt^n \tag{2}$$

The second is a second order equation proposed by Shott[10], it was successfully used to predict the swelling in acrylate polymers by Katime et al. [11], which is:

$$\frac{dS_w}{dt} = k(S_{w\infty} - S_w)^2 \tag{3}$$

Where  $S_w$  and  $S_{w\infty}$  are the hydrogels retained water at time *t* and at the equilibrium swelling state, respectively, and *k* is a swelling rate constant. Integration of the equation 3 produces the following equation:

$$S_{w} = \frac{kS_{w\infty}^{2}t}{1+kS_{w\infty}t}$$
(4)

The previous mathematical expression can be rewritten as a linear equation for *t*, given:

$$\frac{t}{S_w} = \frac{1}{kS_{w\infty}^2} + \frac{t}{S_{w\infty}}$$
(5)

This equation is similar in order like chemical kinetics relationships.

#### **Results and Discussion**

Figure 1 shows the amount of solution diffused inside the PAA beads at different concentrations, it was found that a greater amount of DGA, lower absorption of the diffusing solution. This is because DGA increases the viscosity of the solution. Also it is clear that a bigger time, greater the amount of absorbed solution.

Figure 2 shows the Raman spectra of particle obtained with the solution A. There are peaks at  $1010 \text{ cm}^{-1}$  for S = O bond of the sulfonic group. The peaks at 765 cm<sup>-1</sup> are due to the propyl C-H bond and the peaks of 560 and 496 cm<sup>-1</sup> correspond to C-C bonds of to the DGA. The height of these peaks decrease with deeper inside of the particle was done the analysis, so that we can infer that it is due at the chemical gradient on the particle caused by the process of synthesis [12].



*Figure 1.* Absorption of SMP/DGA solution by crosslinked PAA as a function of time of immersion at different concentrations

Figures 3a, 3b and 3c, shows the swelling kinetics for hydrogels obtained at different concentrations as a function of SMP/DGA diffusion time. In accordance with diffusion time increases, the capacity of hydration decreases, which is due to greater presence of crosslinked material. The cross-linked interpenetrating polymer absorption has been extensively studied in recent decades, and the work in this research field has generated a high level of knowledge about the transport phenomena in these materials [13]. Nevertheless the cross-linked interpenetrating polymer absorption is different from the behavior of crosslinked hydrogels that were sinthetized and analyzed in this work. It is due to their significant dimensional increase in the presence of liquid media like water. The dimensions change in the aqueous medium can be expressed as an isotropic swelling, whose overall dynamics can't be described in terms of the Fick's diffusion law, although a kinetic chemical like model presents good concordance with experimental behavior. For our case we employed the Schott's model. In the Figure 3d, 3e and 3f can be appreciated the

swelling of hydrogels as function of time and also can be observed the linear behavior of the materials. For the mathematical treatment we used the ORIGIN 6.0 program. The constant K values for all evaluated systems are show in the Table 2, where the linearity factor obtained for each correlation shows the perfect match of model.



Figure 2. Raman spectra as a function of the radius of penetration, particle A20

Hydrogels	Maximum	$K \times 10^{2}$	Linearity
	Swelling		Factor
0 (PAA)	166.0	0.611	0.997
A5	125.4	0.795	0.998
A10	112.0	0.900	0.997
A15	102.5	0.988	0.996
A20	95.8	1.064	0.998
B5	106.0	0.954	0.994
B10	93.0	1.072	0.995
B15	86.0	1.168	0.996
B20	77.5	1.304	0.995
C5	111.4	0.930	0.995
C10	97.9	1.068	0.994
C15	86.2	1.235	0.995
C20	73.3	1.393	0.994

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*Figure 3.* Swelling of hydrogels a) series A, b) Series B, c) Series C as function time. d), e) and f) model second order.

## Conclusions

Hydrogels of poly (AA / SMP-co-DGA) were synthesized and characterized, with a composition gradient through the particle structure, whose was identified by Raman spectroscopy. It was observed that the greater presence of SMP-co-DGA, decreased hydration. A second order sewlling equation showed it is a good model for the kinetics of swelling of these materials

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## SYNTHESIS AND CHARACTERIZATION OF SUPERABSORBENT HYDROGELS (PAA/NAOH-H2O) FOR REMOVAL METAL OXIDE SURFACES

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More recent studies about hydrogels with respect to metals have been studied in aqueous solutions as the absorption of copper ions in copper sulfate solutions [1], ion absorption of nickel, magnesium and iron, in treated water industry automotive [2], absorption of copper ions, nickel and cobalt from solutions of copper sulphate, nickel chloride and cobalt sulfate [3]. This motivates the development of research in the removal of metal oxides on surfaces.

In the project presented the synthesis method to obtain hydrogels is an important factor, however the discussion of the results obtained by performing absorption experiments, indicate the maximum metal removal obtained depending on the variation of percentage of initiator, cross-linking and neutralization. These experiments include tests of swelling in solutions of different pH on metal oxide surfaces, as well as a characterization of the properties of the hydrogels by atomic absorption spectrophotometry (AA), thermogravimetric analysis (TGA), Differential Scanning Calorimetry (DSC ), Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), viscometry.

The molar ratio of neutralizing the monomer, the percentage of inbreeding and rate of initiator used in the reaction influences the molecular weight, thermal behavior, swelling rate and capacity for removal of metal oxides on surfaces like answers to these variations. Absorption of metal oxides is favored by a lower percentage of crosslinking that this allows greater absorption of water because it has more space between the polymer chains.

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# N-ISOPROPYLACRILAMIDE/ITACONIC ACID HYDROGELS FOR THEOPHYLLINE RELEASE

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## Abstract

In this paper we present the release of theophylline from hydrogels of poly (N-isopropylacrilamide-co- itaconic acid) as a function of pH. The hydrogels were synthesized by copolymerization of N-isopropylacrilamide and itaconic acid in aqueous solution using a weight ratio of 85/15 and as crosslinking agent the N, N-methylenebisacrylamide. The hydrogels were purified and then loaded with theophylline using saturated solutions of the drug. Once loaded the hydrogels, their drug release at 38 ° C in aqueous solutions was determined at different pH's which correspond to the pH conditions of the intestinal tract (1.2, 4.5, 6.5). It was found that increasing the pH, the amount of drug released and the release rate increases

## Introduction

Hydrogels are polymers that are insoluble in water, soft, elastic and swell in the presence of water increasing their volume, while maintaining its shape. Some of the polymeric hydrogels present a phase transition, allowing them to be used in biomedical applications [1,2]. Depending on the monomers used, the phase transition of the polymeric hydrogels can be induced by changes in temperature, pH, solvent composition and other system conditions [3-5].

Hydrogels synthesized using the monomer N-isopropylacrylamide (NIPA) show a response with temperature, that is, by increasing the temperature there is a gradual decrease in their water absorption capacity, until they reach a temperature where they show a drastic decrease in their capacity to absorb water [6,7]. This phase transition results from the decrease of the interactions between the amide groups and water and the increase of the hydrophobic interactions[8]. When using ionizable monomers it is possible to obtain a pH-sensitive hydrogel (swelling capacity changes with pH) [5,6,9].

Because of their volume change (collapse and swelling) that present the hydrogels when some of the properties of the medium in which they are immerse are modified, they are considered as "*smart materials*". The knowledge of the kinetics of swelling-collapse of the hydrogels is an important factor in the design of devices for drug release [7]. In this work we report the synthesis of hydrogels of poly (NIPA-co-itaconic acid)and their behavior in drug release. The hydrogels were used to release theophylline, which was loaded into the hydrogels and released at 37°C at different pH's.

## Experimental

## Synthesis

The monomers, itaconic acid (IA) with a purity of 99% and N-isopropylacrylamide (NIPA) with a purity of 99% were obtained from TCI, the initiator potassium persulfate (KPS) with a purity of 99%, N, N, N, N, N'-tetramethyl-ethylenediamine (TMEDA) used as an accelerator, and N', N'-methylenebisacrylamide (NMBA) used as crosslinker, with a purity of 99.5%, were obtained from

#### MACROMEX 2011

JT Baker. The hydrogels were prepared using 2.0 g of a mixture of NIPA monomers/AI in a weight ratio of 85/15 and 0.02 g of crosslinking agent. This mixture was dissolved in 18 grams of water; nitrogen was bubbled for two minutes to remove dissolved oxygen. To start the reaction the initiator and accelerator are dissolved in 1 ml of water (1% based on the weight of the monomers) and the mixture was allowed to react for one day at 25 °C. Upon completion of the reaction, samples were dried to constant weight by placing them in a vacuum oven at 45 °C. To remove the unreacted chemicals, the hydrogel is placed in double-distilled water at 25 °C for three days (time to reach equilibrium swelling). Then the samples are transferred to a distilled water bath at 45 °C where the hydrogel collapses and expels water, this process is repeated four times and then dried to constant weight in a vacuum oven at 45 °C.

**Charge of the drug**. Once dried, hydrogels were weighed, then placed for 24 hours in 20 mL of an aqueous solution of theophylline at 23  $^{\circ}$  C with a concentration of 10 mg /mL, leaving in solution for 24 hours. To determine the amount of theophylline loaded, the hydrogels were removed from the solution and dried to constant weight.

Syntheses of polyethers were achieved by polycondensation (Table 1). Dense polymer films were prepared by casting from  $CHCl_3$  solutions, containing 10% (w/v) polymer onto glass plates and dried overnight at room temperature. They were removed from the glass plates and dried for another 24 h at 60°C under vacuum in order to evaporate residual solvent.

#### Drug release.

The hydrogels containing the thiophylline were placed in 900 ml of at 37 ° C in aqueous solutions with three different pH's (1.2, 4.5 and 6.5). To obtain the desired pH, the guidelines of the Mexican Pharmacopoeia were followed. Hydrochloric acid was used to obtain the pH 1.2, citrate for pH 4.5 and phosphates for pH 6.5. The drug release experiments always maintained Sink conditions. The sampling times were: 10, 15, 20, 30 minutes, 1, 2, 4, 6, 8, and 24 hours. Aliquots (5 ml) were taken and its absorbance was determined on a spectrophotometer UV/V at a wavelength of 270 nm.

## **Results and Discussion**

Figure 1 shows the release of thiophylline from hydrogels of poly (NIPA-co-IA) when the samples were loaded at 25 ° C, dried and placed to release the drug in aqueous solutions at 37 ° C at three pH values (1.2, 4.5 and 6.5). These pH values were selected to simulate pH conditions in the intestinal tract (stomach, small intestine and large intestine). When introducing the loaded xerogels in the aqueous solutions begin to swell by absorbing water and to release the drug. At pH 1.2 (stomach conditions) the rate of drug release is practically constant and after 24 hrs the total amount released is small (14.2%), under the conditions of the small intestine (pH = 4.5) the initial drug release rate is high and after 8 hrs it decreases and remains almost constant. At pH 6.5 (large intestine conditions) the drug release behavior is similar to that of pH 1.2, it is practically constant and after 24 hrs the total amount released is small (19.9%). Since physiological conditions establish the place where the major part of the drug is released, it is important to consider the relationship of the drug pKa with the pH of the medium (gastric or intestinal) because only the ionized fraction of drug is absorbed.



#### Conclusions

Hydrogels of poly (NIPA-co-IA) sensitive to pH and temperature were loaded with teophyline. It was found that most of the drug is released at a pH of 4.5 which corresponds to the conditions prevailing in the small intestine; these conditions allow having a large fraction bioavailable, ie the amount of drug in blood relative to the dose contained in the hydrogel.

#### Acknowledgements

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# CONTROLLED RELEASE OF UREA FROM HYDROGELS OF ACRYLAMIDE-CO-ACRYLIC ACID/HYDROXYETHYL STARCH

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Currently there are several national programs to address the growing demand for fertilizers. The ideal fertilizer is one that provides essential nutrients, such as nitrogen, phosphorus, potassium and zinc; preferably with reasonable water retention. The fertilizer should find that the matrix to carry out a release at low release rates. On the other hand, it is intended that the fertilizer is released from friendly materials to the environment, so in this work are carried out the synthesis, characterization and release testing.

Hydrogels are polymers that are capable of altering his arrangements and extensions in space in response to any effort to be submitted. The chains are linked by covalent bonds that form knots or crosslinking points. Density of nodes is called the number of crossover points per unit volume is in the material. In the case of cross-linked polymers, the molecular knot formed by covalent bonds determines the network. The appearance of a gel depends on the ration liquid/solid. In the case of crosslinked polymers, gels have an aspect of elastic solids.

In 2005, Helaly et al.[1], reported the slow release of urea from polymeric hydrogels of acrylamide with acrylic acid and maleic acid. In this work we carried out the experiments and calculations needed to determine the diffusion coefficients from the copolymer raised.

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# SORPTION STUDIES OF CUPPER (II) IN CRYOGELS FROM CHITOSAN AND CELLULOSE

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#### Abstract

Metals differ from other pollutants owing to their chemical transformations and because they are not biodegradable (metals bioaccumulate in organisms causing damage to biota and groundwater) [1] [2]. Biosorption is a method utilized for removing heavy metals using natural materials [3], such as chitosan and cellulose, which have shown to be efficient in sorption of metals [4]. Cryogels are materials made up of interconnected macroporous grid with a considerable surface area, these characteristics together with those of raw materials used to synthesize, offer a promising use as biosorbents. This paper focuses on presenting the results of the study of sorption of Cu2+ ions in aqueous solution with a Q-EGDE-C cryogel. In order to define the working conditions, first the influence of variables such as the pH solution was analyzed, then the sorption kinetics experiments were carried out as well as the application of pseudo second order to the data, in order to determine if this procedure describes the behavior. Finally, the same was made in the realization of the sorption isotherms experiments using Langmuir and Freundlich models.

#### Introduction

The sources of heavy metals in the environment are large, not only discharges from mines produce these pollutants, but also urban waste water and sludge obtained after their purification, which in many places have been used as fertilizers without worrying about the high content of contaminants [5]. They differ from other contaminants because they are not biodegradable, undergo chemical transformations and their potential toxicity to living organisms generate high economic, environmental and public health impact [2], as in the case of  $Cu^{2+}$ ,  $Cd^{2+}$ , and  $Co^{2+}$  [6, 7]. Adsorption is a process whereby material is removed from one phase and concentrates on the surface of another phase (usually solid). This phenomenon is an excellent way of removing contaminants because unwanted components are removed from a fluid mixture, furthermore, the amounts withdrawn may be very high compared to other methods [8]. Available materials used in the sorption processes are different. Macroporous arrays and three-dimensional structures have been recently studied for this purpose. The chitosan and cellulose are two polysaccharides known for their adsorptive properties so these biopolymers were used in this work to synthesize a cryogenic material with interconnected macroporous structure and assess their ability to the sorption  $Cu^{2+}$  present in aqueous solutions.

## Experimental

Cryogel synthesis. Synthesis of chitosan-ethylene glycol diglycidyl ether-cellulose (Q-EGDE-C) cryogel, was reported previously [9]. The synthesis started from the obtaining of a chitosan-cellulose hydrogel (QC) which was crosslinked with ethylene glycol diglycidyl ether (EGDE), after that, it was subjected to a freezing process, and then dried by lyophilization, obtaining Q-EGDE-C cryogel.

Sorption experiments at different pH. Six copper solutions were prepared in duplicate, with an initial concentration of 20 mg / L of Cu<sup>2+</sup> and an initial pH value of 3, 4, 5, 6, 7, 8. These solutions were prepared from a copper standard solution Fluka and used Analytical solutions of HCl 2N and 2N NaOH to adjust pH to specified values. Then approximately 0.170 g of the adsorbent material Q-EGDE-CL was weighed (the hydrated cryogels dried superficially with filter paper before each weighing) and added to containers of high-density polyethylene (HDPE) with a capacity of 30 mL, after that each container was added to 20 mL of copper solution to a given pH value. The containers were placed on an orbital shaker Heidolph Unimax branded 1010 to 25 ° C and 150 rpm for 12 hours. Then supernatant was filtered on a millipore Kit and added 10µL of ultra pure HNO 3 to maintain that the ions remain in solution as well as to quantify the amount of Cu<sup>2+</sup> ions adsorbed. The samples were sheltered in the refrigerator to be analyzed after by atomic absorption.

Kinetics of sorption. To determine the time at which the process reaches equilibrium sorption, approximately 0.170 g of cryogels Q-EGDE-CL hydrated were weighed and then added to HDPE containers after this, 20 mL of metal solution (at a concentration of 20 ppm) was added to each container. The containers were placed on an orbital shaker at 25 ° C and 150 rpm during time intervals from 5 min to 48 hours. Then supernatant was filtered and conditioned to ensure that the sample ions remain in solution until the quantification of  $Cu^{2+}$  ions sorbed. After obtaining the concentrations from the supernatants, sorption capacities were calculated for each one of the contact time by the Equation 1 and obtained the parameters fit kinetic model pseudo-second order of Ho.

$$q = \frac{\left(c_i - c_f\right) * V}{m} \tag{1}$$

Adsorption isotherms. The adsorption equilibrium of copper ions was studied through batch experiments with two replicas at pH value of 6, an equilibrium time of 600 min and constant temperature of  $25^{\circ}$  C. 20 mL of aqueous solution of copper with concentrations of 1, 4, 8, 12, 16, 20 mg / L and a pH of 6 made contact with an amount of about 0.170 g of Q-EGDE cryogels -CL for it, 0.170 g of the adsorbent material (the hydrated cryogels dried superficially with filter paper before each weighing) were approximately weighed and added to HDPE containers, each container containing 20 mL of the solution at different concentrations of metal ions copper (II). The containers were placed on an orbital shaker at 25 ° C and 150 rpm during equilibration time. Then supernatant was filtered and added 10µL of ultra pure HNO3. The samples took shelter in the refrigerator until further analysis by atomic absorption. Finally, the adsorption capacity was calculated using Equation 1 and experimental data were fitted to Langmuir model (Eq. 2) and Freundlich (Eq. 3) shown below:

$$q_e = \frac{q_{e\max}bc_e}{1+bc_e} \tag{2}$$
$$q_e = k_F c_e^{\frac{1}{n}} \tag{3}$$

The quantification of  $Cu^{2+}$  in the supernatants of all sorption experiments were carried out in a equipment of atomic absorption at flame, model AAnalist Absorption Spectrometer mark Perkin Elmer, the wavelength was 228.80 cm<sup>-1</sup> with a mixture of air-acetylene flame.

## **Results and Discussion.**

Sorption experiment at different pH's. Figure 1 shows a graph which presents the effect of pH on the sorption capacity of copper ion, where the sorption capacity depends on the pH of the aqueous solution of copper. However, it is known that divalent copper species is a complete solubility in aqueous media at pH 6 and below, so this value was determined as suitable for kinetic experiments and sorption isotherms with cryogels Q-EGDE-CL in aqueous solutions of copper.



Figure 1. Effect of initial pH on the sorption of copper ion at 25 ° C.

Sorption kinetics. Figure 2 shows the kinetics of copper at 25 ° C, where increasing values of removal are observed during the first 300 min with a corresponding value of  $q_t = 20.89 \text{ mg} / \text{g}$  at this time, this value tends to stabilize during the next 180 min, however, sorption of copper increases to a maximum value of  $q_t = 22.40 \text{ mg} / \text{g}$  at 720 min, so the sorption capacity is a function of time.



Figure 3 shows the comparison between experimental values and values calculated by the Ho model for the kinetics of adsorption at 25 ° C. The data shows that between 5 and 720 min fit, a along a line with an  $R^2$  value of 0.9908, which is able to obtain the rate constant of pseudo second order  $k_2$  (min<sup>-1</sup>). Noting that parameters of correlation coefficients reported in Table 1 shows that the kinetic model of pseudo second order satisfactorily reproduce the experimental results with a correlation coefficient value of 0.9908, a maximum sorption capacity of 22.4 mg /

Second US-Mexico Meeting "Advanced Polymer Science" and XXIV SPM National Congress Riviera Maya, Q. Roo, México. December 2011 g for the kinetics at 25  $^\circ$  C. Ho model indicates that the sorption of  $\mbox{Cu}^{2+}$  was done via chemical interaction.





Parámetros	
$\mathbb{R}^2$	0.99
k <sub>2</sub>	0.0014 g mg <sup>-1</sup> min <sup>-1</sup>
q <sub>e</sub>	22.4 mg g <sup>-1</sup>

Table 1 Parameters Ho Model for the kinetics at 25  $^{\circ}$  C

Adsorption isotherms. Figure 4, 5 and table 2 presents the results obtained. Comparing the parameters of correlation coefficients reported in Table 2 show that both models reproduce the experimental results of the isotherm in an acceptable manner, but is the Freundlich model which best reproduces the data. The values obtained from  $K_F$  and n (Freundlich constant), related to the affinity of the biosorbents for metal ions and the intensity of adsorption respectively, demonstrate an affinity of biomass to copper, were obtained as higher values of n 1.0, so the strength of metal sorption by biosorbents is intense, which represents a favorable sorption.



Figura 4. a)Langmuir and b)Freundlich linearized models

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Figura 5. Comparison of data calculated, using the model of a) Langmuir and b) Freudnlich and experimental data of sorption isotherm of copper at 25 ° C

Models	Ecuation	Parameters
		25 °C
Langmuir	$q_{e,max} bC_e$	$R^2 = 0.9908$
	$q_e = \frac{1}{1 + bC_e}$	$q_{emaz} = 19.5 \text{ mg g}^{-1}$
	C C	$b = 0.7 L mg^{-1}$
	$\frac{1}{n}$	$R^2 = 0.9908$
Freundlich	$q_e = K_F C_e^n$	$K_{\rm F} = 6.1$
		n = 1.7

#### Conclusions

Through sorption kinetics was observed that the process was carried out quickly within the first 300 minutes and the adsorption equilibrium is reached from 420 to 500 minutes. The kinetic model of pseudo-second order adjusted better the experimental kinetic data. This model proposes that the sorption mechanism is second order (chemical adsorption takes place). With respect to the isotherms, the model that best fitted the experimental data was the model of Freundlich isotherm, which assumes that the surface of the sorbent is heterogeneous and that the positions have different sorption affinities, so that takes after the formation of multiple layers.

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#### MACROMEX 2011

# FILMS OF CHITOSAN AND POLIVYNYL ALCOHOL WITH CALIX [4] PYRROLE FOR RECOGNITION OF NITRITE.

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#### Abstract

Films of Chitosan (CS) and Polyvinyl Alcohol (PVA) containing different concentrations of meso-octamethyl-calix [4] pyrrole were prepare for anionic detection and recognition studies using UV-Vis spectroscopy. Thin films were prepared from aqueous solutions of PVA/calix pyrrole and chitosan/calix pyrrole mixtures and were tested for NO<sub>2</sub><sup>-</sup> anions detection. CS films showed higher absorption ability compared to PVA films and one possible explanation is that PVA films are insoluble in NO<sub>2</sub><sup>-</sup> aqueous solutions while CS films are moderately soluble. Our results show that these films are potentially attractive for anionic sensors application specifically in food industry for NO<sub>2</sub><sup>-</sup> anions recognition.

# Introduction

Nitrate and nitrite are ubiquitous within environmental, industrial, physiological and food systems [1].  $NO_3^-$  and  $NO_2^-$  are potentially toxic and have raised numerous concerns; these problems have been widely recognized, and as a consequence, statutory frameworks aimed at controlling their level within the wider environment and within food products have been imposed in most industrialized countries [1]. Particularly, nitrites in meat are used for bacterial action during processing and storage; however, at high concentrations they are potentially toxic. Because of this, the monitoring of these ions has increased attention and as a consequence, statutory frameworks aimed at controlling their level within the wider environment and within food products have been imposed, contributing to ease some of the apprehensions raised by the medical community.

Calix pyrroles, an easy-to-make class of macrocycles, are effective and selective receptors for anions in solution and solid state [2]. Their anion recognition characteristic which has been previously demonstrated with different anions such as fluoride, bromide and chloride has attracted extensive interest [3].

On the other hand, Polyvinyl Alcohol (PVA) and Chitosan (CS) are widely used in packaging and coating in the food industry due to their film forming ability and in the case of chitosan to its antimicrobial activity [4].

Because of the explained above, this work proposes the combination of the individual properties of these components to obtain films with potential application as food products anion sensors. The ability of nitrite recognition of PVA and CS with different concentrations of calix[4]pyrrole films is analyzed by UV-Vis spectroscopy. The combination of the anion recognition ability of

calix[4]pyrrole (C[4])and the easy preparation of the proposed polymers films, joined to the antibacterial activity of chitosan are very attractive in anionic species detection and recognition, and this area is viewed as a promising area of study for the environmental and biological development related to sensors.

# **Experimental**

# Synthesis of meso-octamethyl-calix [4] pyrrole.

1 eq of pyrrole was mixed with 0.25 eq of bismuth nitrate and stirring at room temperature. Ketone was also use as solvent; the reaction was stopped when the sub products appeared on TLC (1.5 h). The calix [4] pyrrole (**Figure 1**) was obtained with 79% yield [5] and it was corroborated by <sup>1</sup>HNMR spectra.



Figure 1. Schematic illustration of Synthesis of Calix [4] pyrrole.

# Film preparation

Chitosan (CS) medium molecular weight (Mw= 150,000 g/gmol) and 82 % of degree of deacetylation (DD) reported by the supplier, was purchased from Sigma-Aldrich. Acetic acid from J.T. Baker was used as received. 1 wt % of chitosan was dissolved into a 0.4 M aqueous acetic acid solution with subsequent stirring during 24 hours to promote dissolution. While Polyvinyl Alcohol (PVA) was dissolved into distilled water at 90°C during 24 hours.

CS/calix [4] pyrrole and PVA/calix [4] pyrrole films were obtained by the following fashion: the proper quantity of calix [4] pyrrole (2 and 3% w/w chitosan dry base and PVA dry base in each case) was poured into the corresponding solution, stirring and further sonicated during 30 min to obtain a homogeneous solution. Afterward, each mixture was poured into different plastic Petri dishes and drying at 60°C during 24 hours in the oven. After solvent evaporation, films of about 30  $\mu$ m thickness were obtained. Rectangular small pieces (1cm × 1cm) were prepared for UV-Vis analysis.

# **Absorption experiments:**

The absorption ability of these films was analyzed for Nitrite Standard Aqueous Solution Merck (stock solution 1000 ppm, 0.02M), prepared with deionized water at 50 and 100 ppm from the stock solution.

One small square of each film (CS 2% calix, and PVA 2% calix) were weighed and poured into different vials with 4 ml of the corresponding dissolution of nitrites (i.e 50 or 100 ppm nitrite concentration), and placed in a water bath at 25°C and stirred for different periods of time.

#### (Table 1.)

After elapsed contact time, the nitrite solutions were analyzed in a UV- Vis Spectrophotometer Agilent 8453.

Table 1. Film whit different concentrations of NO<sub>2</sub> and variations of time: (A) Films of PVA 2% C[4], (B) Films of CS 2% C[4].

(A)			<b>(B)</b>		
Film	NO <sub>2</sub>	Time (h)	Film	NO <sub>2</sub>	Time (h)
PVA a 2%	100ppm	0.5 h	CS a 2%	100ppm	0.5 h
PVA b 2%	100ppm	1 h	CS b 2%	100ppm	1 h
PVA c 2%	100ppm	1.5 h	CS c 2%	100ppm	1.5 h
PVA d 2%	100ppm	2 h	CS d 2%	100ppm	2 h
PVA e 2%	100ppm	4 h	CS e 2%	100ppm	4 h
PVA f 2%	100ppm	19 h	CS f 2%	100ppm	19 h
PVA g 2%	100ppm	21 h	CS g 2%	100ppm	20 h

## **Results and Discussion**

The incorporation of C[4] to CS and PVA solutions produce clear, thin and macroscopically homogeneous films, indicating no apparent phase separation between polymer and macrocyle during the composite film formation.

After elapsed contact time, the nitrite solutions were analyzed by UV-Vis measurements. The UVspectra show an absorption peak at 310 nm corresponding to  $NO_2^-$  ions.

The amount of absorbed anions [q (mg/g)] on the surface of both films was calculated by a mass balance according to Equation (1)

$$q = \frac{V}{W} [Co - Ce] \tag{1}$$

Where Co and Ce are the anion concentration in the initial and the final solution (mg/L) respectively; V is the volume of the solution containing the anion (L); and W is the weight of the PVA or CS film (g).

Absorption amounts *versus* time for both types of films are summarized in Figures 1 and 2.



Figure 1 shows that in CS/C[4] films anion recognition is evident at 0.5 h, and the absorption ability doubles after 1 h. While there is a desorption at 1.5 h, however at 2 h it increases again and it last for 2 more hours up to 4 h after the initial time and finally in subsequent hours the recognition notoriously decreases.

Figure 2, shows the results for UV-Vis absorption analysis in PVA/C[4] films. At 0.5 h anion recognition arises but it is lower compared to that in CS/C[4] films, in this case, the highest absorption occurs after 2 h to finally decreasing continuously in subsequent hours.

It can be seen that the absorption trend in both cases seem to be unstable, probably because the macrocycle at 1 h in the case of CS/C[4] films and at 2h in PV/C[4] films reaches the absorption saturation point, following by the anion discharge. It is noteworthy that the binding properties of the macrocycle are given by weak forces such as hydrogen bonding [7].

From the absorption experiments, it is clearly observed that CS/C[4] films show higher absorption ability than PV/C[4] films, this can be ascribe to two possible factors: in one hand CS/C[4] films are thinner and less rough than PV/C[4] films, this can be ascribe to the fact that CS could be promoting to calyx pyrrole to adopt the cone conformation which is typically adopted for anion recognition. And on the other hand, CS/C[4] films are more hydrophilic which leads to higher swelling and interaction between C[4] and the anion, therefore better absorption.

The size (diameter 3.58 A) and shape (trigonal planar) [1] of the anion may be contributing to its recognition by C[4] and after few hours it delivers the anion. Many studies revealed that C[4] have a strong preference for fluoride ion (one of the smallest and spherical) relative to other anionic guests, such as Cl-, Br- or  $H_2PO_4^{-}[8]$ .

The Mexican legislation (NOM-213-SSAI-2002) establish that the maximum limit of nitrites in meat products is 150 ppm or mg nitrite/kg plus 150 ppm or mg nitrate/kg for unheated meat products. That is a maximum of 300 mg nitrite + nitrate/ kg may be in a batter or a piece of raw ham. Many countries have similar regulations [9,10]

# Conclusions

Preparation of Calix[4]pyrrole, CS and PVA composite films was successfully achieved and their absorption ability of  $NO_2^-$  anions was analyzed by UV-Vis measurements. The absorption studies show that CS/C[4] films exhibited excellent absorption properties, while PVA/C[4] films are poor absorbents compared to CS/C[4] films.

It was noticed that PVA/C[4] films are more resistant to the  $NO_2^-$  aqueous solution than CS/C[4] support. The combination of calyx [4] pyrrole with CS and PVA is a useful approach for the recognition and absorption in a few hours of  $NO_2^-$  anions from aqueous solutions, and they could be used as sensors in the food industry.

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# A STUDY OF THE FRACTURE BEHAVIOR OF A THERMOPLASTIC-MODIFIED EPOXY RESIN REINFORCED WITH CARBON FIBERS

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Epoxy matrix composites reinforced with carbon fibers offer excellent stiffness/weight and strength/weight ratios are suitable for highly demanding structural applications. However one of the disadvantages of these composites is their poor fracture toughness exhibited by epoxy resins [1], because of their high degree of crosslinking. A number of attempts to improve the fracture toughness of these structural materials have been proposed. One of these approaches is the use of tough materials in the matrix such as rubbers or thermoplastic polymers [1, 2].

In this study the fracture behavior of a composite materials based on a thermoplastic-modified epoxy resin reinforced with continuous carbon fibers for two levels of fiber-matrix adhesion was determined. The toughness was determined using the double cantilever test together with surface analysis after failure using SEM. The presence of polysulfone particles improves the fracture behavior of the composite but fiber-matrix adhesion seems to play a very important role on the performance of the composite material.

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# EFFECT OF THE FIBER SURFACE TREATMENTS ON THE INTERFACIAL SHEAR STRENGTH OF POLYSULFONE MODIFIED EPOXY RESIN-CARBON FIBERS.

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Epoxy resins are extensively used in structural applications because of their high performances, such as good mechanical, thermal, and electrical properties. However, further growth of these highly crosslinked materials are limited because of their inherent brittleness, which has led to extensive research efforts to improve their low toughness. In the later years, adding high performance engineering thermoplastics, such as poly(methyl methacrylate), poly(ether sulfone), and polyimide, to the epoxy resins has often been used as a way to solve this problem. Because of their high modulus and Tg, the modified resins can show an obvious increase of toughness but no significant decrease of mechanical and thermal properties. By other hand, the interfacial shear strength between fibers and resin is one of the important factors for determining the usefulness of composite materials. The interfacial shear strength can be affected by the type of fiber and matrix as well as the condition of the fiber surface treatment. In this study, we analyzed the effect of the incorporation of a UDEL 1600 polysulfone to the interfacial shear strength of a EPON 828 epoxy, cured with MPDA, and Hexcel IM7 carbon fibers with three adhesion levels: 1) as received, 2) treated with HNO3 and 3) HNO3 and silanized with z6040 silane (Dow Corning) The IFSS was determined using the microdroplet test. The results of the ANOVA analysis show that both the thermoplastic modifier and the CF surface treatment are significant. It was found that the higher IFSS corresponds to the polysulfone-modified epoxy-silanized carbon fiber.

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# PREPARATION AND CHARACTERIZATION OF AN EPOXY RESIN TOUGHENED WITH POLYDIMETHYLSILOXANE-GLYCYDYL TERMINATED.

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#### Abstract

An epoxy resin was synthesized by reacting diglycydyl ether of bisphenol-A (DGEBA) with 1,2-diaminocyclohexane, (1,2-DCH) added with polydimethylsiloxane-diglycydyl ether terminated (PDMS-DGE). Both DGEBA and 1,2-DCH were well mixed and PDMS-DGE was added as needed to get 0, 5, 10, 15, and 20 parts per hundred of resin (pph) of this additive. Each one of the mixtures was cured in a DSC equipment to obtain the trace of the exothermal reaction. Also, rectangular bars were prepared by curing the mixtures at fixed temperature from 90 to 140 °C and their mechanical properties were measured by using a dynamic mechanical thermal analysis (DMTA) apparatus. Scanning Electronic Microscopy (SEM) was applied to characterize the morphology of these samples after cryogenic fracture and extracted with acetone. It was observed that elastic modulus decreases with content of PDMS-DGE up to 15 pph of this additive, and all these mixtures show phase separation as observed by SEM. Additional experiments were carried out by heating mixtures of 1,2-DCH with PDMS-DGE at 90 °C for 30 min; after cooled to 50 °C, DGEBA was added and curing in DSC. Since their thermograms give a lower in value enthalpy than that of the samples prepared by the above procedure, it is assume that some extent of reaction took place during the applied preheating.

#### Introduction

Epoxy resins are used in many industrial applications because of their excellent properties: low shrinkage, outstanding adhesion, good electrical insulation and chemical resistance. For their use as rigid matrices in semiconductor industry and advanced aerospace materials, epoxy resins must overcome some disadvantages such as brittleness, which arises from the high extent of crosslinking, and flamability [1-4]. To reduce such brittleness epoxy resins have been toughened by adding inert or reactive polymers, such as thermoplastics and elastomers without affecting properties as Tg and stiffness [5-8]. The cure state of thermosetting is the extent at that the crosslinking has advanced throughout the polymer network. The crosslinking density and conversion determine the cure state and, therefore, the mechanical properties of the resulting network. As the reaction proceeds, two distinct phenomena, gelation and vitrification, become determinants of the cure process of thermosetting materials due to diffusional control of further reaction. If polymeric additives are miscible with the epoxy matrix, the resulting system is of the type of semi-interpenetrating polymer network (s-IPN) with enhanced mechanical properties such as tougheness [7,8]. This property may also be increased by addition of some immiscibe polymeric additives, which tend to segregate during the curing process, and this thermodynamic factor, as combined with the kinetics of curing process, has a strong influence on the phaseseparated extent and the size of microdomines. Thus, a good control of several conditions is needed to get a full cure by avoiding vitrification before a high conversion, for which the  $T_{cure}$ must be always higher than the Tg that resin eventualy would have after a full conversion. Besides of these factors, a well control of the size of phase separated and its distribution are required to provide a good tougheness of epoxy resins.

# **Epoxy resin synthesis**

Diglycydyl ether of bisphenol-A (DGEBA) and 1,2-diaminocyclohexane (1,2-DCH) were well mixed by stirring at 50 °C for 30 min. Then, polydimethylsiloxane-diglycydyl ether terminated (PDMS-DGE) was added in 5, 10, 15, and 20 pph.

In additional experiments, 1,2-DCH was mixed with PDMS-DGE as needed to obtain 5, 10, 15, and 20 pph in the final resin. These mixtures were heated at 90 °C for 30 min in order to allow some extent of reaction between the amine groups of the former with the glycydyl groups of the latter. Samples of these and the above mixtures were taken to be cured by differential scanning calorimetry (DSC) and obtain their enthalpy of reaction.

# Samples preparation

The above mixtures were also cured at 90, 100, 110, 120, 130, and 140 °C for 30 min in a vacuum oven to prepare samples for measuring the dynamic mechanical properties. These samples were rectangular in shape of 40 x 11 x 3 mm<sup>3</sup>. Samples for scanning electronic microscopy (SEM) by cryogenic fracture of the above samples in liquid nitrogen.

# Characterization

DSC runs were carried with an DSC 2920 apparatus from TA Instruments at 10 °C/min under nitrogen from room temperature to 200 °C. The enthalpy of reaction was measured on the first run, whereas the Tg was measured on the second run.

DMTA runs were performed by using an DMA TA Instruments 2980 between 50 and 250 °C at 3 °C/min under atmosphere conditions at frequency of 1Hz, and the dual cantilever clamp. SEM images of the surface fracture were obtained with a Carl Zeiss DSM 940A Microscope by using the electron backscattering technique, after the surfaces were covered with gold.

# **Results and Discussion**

Fugure 1(a) shows the DSC thermograms obtained for the curing process of DGEBA/1,2-DCH mixtures containing 0, 5, 10, and 15 pph of PDMS-DGE at 110 °C; the maximum of heat flow decreased with the content of PDMS-DGE, but no effect was observed on the curing time.

Storage modulus (G') of epoxy resin without PDMS-DGE shows a very slight increasing, near 5000 MPa, with the  $T_{cure}$  at which the resins were prepared (Fig. 1(b)). Major effect showed the  $T_{cure}$  on the temperature of initial abrupt decreasing ( $T_{onset}$ ) of storage modulus: the higher the  $T_{cure}$  the higher the  $T_{onset}$ ; from 90 °C for the resin cured at 90 °C, and 120 °C for the resin cured at 140 °C. Similar behavior was showed for Tan delta, since its maximum value was increased from 120 to 140 °C for  $T_{cure}$  from 90 to 140 °C. In contrast, the content of PDMS-DGE (5 and 10 pph) causes a decreasing of the initial storage modulus of the resin cured at 140 °C and an increasing on the  $T_{onset}$  of G', which is an indication of toughening of resin by PDMS-DGE (Fig. 2). However, the resin containing 15 pph did not show the same behavior, since this sample exhibited a higher value for the storage modulus and a lower  $T_{onset}$  of G', similar to that of the sample without PDMS-DGE. This unexpected result was due to some loss of PDMS-DGE, since a part of this additive was drive out from the bulk of resin. The high  $T_{cure}$  (140 °C) applied for this sample was not enough to prevent such drive out; the phase separation was more rapid than the curing process.



Figure 1. (a) DSC thermograms for resins containing 0, 5, 10, and 15 pph of PDMS-DGE cured at 110 °C. (b) Storage modulus of epoxy resin without PDMS-DGE cured from 90 (top labeled ) to 140 °C (bottom labeled).



Figure 2. Storage modulus of resins containing 0, 5. 10, and 15 pph (from top to bottom labeled) cured at 140 °C.

Resins containing 10 pph of PDMS-DGE and cured at temperatures from 90 to 130 °C exhibited an interesting mechanical behavior (Fig. 3(a)); in effect, the initial storage modulus showed a clear tendency to lower values (from 5000 to 4500 MPa) as higher the  $T_{cure}$  (from 90 to 130 °C). In fact, unexpectedly the  $T_{onset}$  of G'showed a notoriously higher values (c.a. 120 °C) than that of the cured at lower temperature (c.a. 95 to 105 °C). On this basis, conditions of  $T_{cure}$  of 130 °C and 10 pph of PDMS-DGE appeared to be better for toughening the studied epoxy resins. Figure 3(b) shows that maximum of Tan delta of resins increased with the content of 0, 5, 10, 15 pph of PDMS-DGE and cured at 140, being the higher increment for that of 15 pph. All the peaks of Tan delta are broader, which indicates an ample distribution of molar mass of segments in the network.



Figure 3(a, leftt). Storage modulus, G<sup>'</sup>, of resins containing 10 pph and cured at 90, 100, 110, and 120 °C. 3(b, right). Tan delta of resins cured at 140 °C containing 0, 5, 10, and 15 pph of PDMS-DGE.

Figure 4 shows the SEM micrographies of the resin containing 5 pph (left) and 10 pph (right) of PDMS-DGE cured at 130 °C, and fractured in liquid nitrogen, then extracted with acetone for 24 h. In both images micro-voids can be clearly appreciated. These voids correspond to zones firstly occupied by PDMS-DGE, and left them free after this additive was drive out by the solvent.





Since the image wide correspond to 180  $\mu$ m, the size of such voids is in the range of 0.6 to 0.4  $\mu$ m. This is a well distribution in size, and the resin containing 10 pph of PDMS-DGE showed a higher density and more uniform distribution of voids.

Respect to the additional experiments in which the PDMS-DGE was heated with 1,2-DCH for 30 min at 90 °C, and then cured with DGEBA, it is interesting to mention that acetone did not extract PDMS-DGE. This result is an indication of a possible reaction of terminal diglycydyl groups of PDMS-DGE with 1,2-DCH during the preheating of the resin. In fact, in this process a slight increasing on viscosity could be appreciated when this mixture was left to cool to 50 °C before the addition of DGEBA. On the other hand, DSC thermograms of these resin containing 5 and 10 pph of PDMS-DGE exhibited an enthalpy of reaction of 390 and 360 J/g, which are lower than that of 470 J/g typical resins of DGEBA with 1,2-DCH. If no reaction of PDMS-DGE would take place with 1,2-DCH, these enthalpy values would be of the order of 445 and 420 J/g. These experiments are being continued in order to establish the influence of temperature of the preheating on the reactivity of mixture of PDMS-DGE with 1,2-DCH.

## Conclusions

Epoxy resins of DGEBA/1,2-DCH was toughened with PDMS-DGE. The better results were obtained for the resins with 5 and 10 pph of PDMS-DGE. SEM micrographies of these samples showed a good size and a well distributions of PDMS-DGE, as observed after this additive was extracted by acetone, with the 10 pph of PDMS-DGE having a higher density of voids. Preliminary experiments indicate that PDMS-DGE can react with 1,2-DCH during a preheating, and this treatment may be used to control de size of microparticules of PDMS-DGE.

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# POLYENE ACCUMULATION AND COLOR CHANGES PRODUCED ON PLASTICIZED PVC FORMULATIONS DEGRADED ISOTHERMICALLY AT DIFFERENT TEMPERATURES OR, AT ENVIROMENTAL CONDITIONS

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#### Abstract

PVC is generally degraded during processing, producing several undesirable effects. In this work, mixtures of calcium and/or zinc stearates and epoxidized soybean oil are used as stabilizers. The formulation composition was systematically varied considering the following parameters: a) presence of epoxidized soybean oil and, b)  $CaSt_2/ZnSt_2$  ratio. Each formulation underwent the following degradation conditions: i) isothermal heating (IH) at 60°C, ii) IH at 120°C, iii) IH at 150°C and, iv) environmental outdoor conditions. The evolution of the concentration of different polyenes (UV-Visible spectroscopy) and the color modifications produced throughout the degradation process are reported. In the most of cases, the degrading behavior of a given sample show a complex dependence on degradation temperature, therefore, the thermal stabilities based on studies at a given temperature cannot be always used to predict the behavior at another degrading conditions.

#### Introduction

Unless it is stabilized, PVC is degraded during processing. Such thermal degradation is the result of a process called "zipper dehydrochlorination", which generates polyene sequences in polymer chains that may produce an undesirable color in the material [1]. In addition, since polyenes are highly reactive, they may react to form crosslinked polymer chains [1], as well as low molecular weight molecules [1-2]. As a consequence of such secondary reactions, the mechanical behavior and the color [1] may be importantly modified. It is generally accepted that stabilizers may react with labile chlorine atoms in PVC chains (preventing further dehydrochlorination) and/or react with the HCl generated by the degradation process (which accelerates the degradation process) [1,3]. K, Ca and, Ba carboxylates are mostly HCl scavengers [1]. However, Zn and Cd carboxylates are able to scavenge HCl and, also, to react with labile chlorine atoms [1]. An undesirable effect of the stabilizing action of zinc stearate  $(ZnSt_2)$  is the production of  $ZnCl_2$ , which can promote the sudden dehydrochlorination of PVC chains. [1, 4-5] However, it has been claimed that such sudden process occurs only after the ZnCl<sub>2</sub> concentration reaches a certain level [5]; in such process, ZnCl<sub>2</sub> is consumed [4]. Besides, it has been experimentally demonstrated that, formulations prepared with mixtures of Zn and Ca carboxylates show a synergistic stabilizing action [6-9], mainly due to the Ca carboxylate, which act as ester-exchangers with ZnCl<sub>2</sub> [1, 6-7]. Epoxidized compounds are recognized as HCl scavengers [1, 8], but can also participate in other stabilization reactions, where they react simultaneously with HCl and ZnSt<sub>2</sub> [8]. In the catalytic presence of ZnCl<sub>2</sub>, epoxidized compounds react with such chloride to produce a chemical compound that is able to remove chlorine atoms in PVC chains through an etherification reaction [1].

# Experimental

The samples to be post-processed were prepared as follows: (a) dry blending the components, (b) pelletizing the dry-blend (twin-screw extruder Leistritz 276L/32D) and, (c) extruding the pellets (to obtain ribbons) Two different di-2-ethyl hexyl pthalate (DEHP)/epoxidized soybean oil (ESO) mass ratios were used: 45/0 or, 45/6. For each one of the DEHP/ESO ratios, the following CaSt<sub>2</sub>/ZnSt<sub>2</sub> mass ratios were used: 0.0/1.0, 0.2/0.8, 0.4/0.6, 0.6/0.4, 0.8/0.2 and, 1.0/0.0; in all formulations the total content of stearates was 1.0 phr. The samples were post-processed by heating at 60, 120 and 150°C, using a force convection oven; the maximum degradation times were, respectively, 44 days, 12 h and 3 h. An additional post-process were carried out by exposition at environmental outdoor conditions; the maximum degradation time was of 182 days. The concentration of polyenes was determined by UV-visible spectroscopy (UV-visible Spectrophotomer Cintra 6 GBC). In addition, the visual appearances of the initial and degraded samples are presented.

# **Results and Discussions**

By space restrictions, in this paper will be only presented and briefly discussed some relevant results. In Figure 1, the approximate colorations of the samples are presented. There, it can be appreciated that, formulations containing more  $CaSt_2$  than  $ZnSt_2$  tend to be reddish, while the other samples tend to remain almost colorless (gravish tonalities in Figure 1) during certain period, abruptly blackening after such period. Besides, in all tested formulations, it is evident the beneficial effect of ESO presence; the respective formulations 45/6 show less intensive colors than the equivalent ones 45/0. In general terms, the color changes produced for the IHs are qualitatively similar among them. Nevertheless, the changes produced by the environmental degradation (ED) follow a different color path. Firstly, when the original samples that underwent to ED are observed, a decrement on the color intensity of all samples can be visually appreciated, during the first weeks of degradation (unfortunately, it cannot be always appreciated on Figure 1). Besides, especially in the "samples 45/0" degraded during 60 days, several intensely colored points can be appreciated, denoting that, a nucleation process is occurring simultaneously to the homogeneous change on color of samples. Finally, in most of tested formulations, the "color trajectories" followed during the EDs are clearly different to the ones observed on the equivalent formulations undergoing IH. Regarding the polyene accumulation behavior, in Figure 2, it can be appreciated the detrimental effect on the "processing thermal stability" produced by the CaSt<sub>2</sub> presence (the  $P_n^o$  values for formulation lacking of CaSt<sub>2</sub> are lower than the equivalent ones for the other two formulations). In addition, it must be mentioned that, the polyene accumulation behavior during EDs behave in a different way than the one observed during IHs. Thus, the IHs produced on samples a linear accumulation of polyenes during the degradation process (the dP<sub>n</sub>/dt values presented in Figure 2). However, in the ED process, the  $P_n$  values decreases during the first weeks of the environmental exposition, therefore, the  $\Delta_{dec}$  parameter was defined as the percentage decrement on the polyene concentration during the first 15 days of environmental exposition; the corresponding  $\Delta_{dec}$  values are also plotted in Figure 2. There, it can be noticed that, important decrements on the amount accumulated of all measured polyenes is occurring during such initial degradation period; this phenomena is characteristic only on the environmental degradation process.

phr.phr 45.0	1.0	T <sub>deq</sub> ,°C↓ 150				~	ESU		17 . A. A. A.	~	v .	0	5		
45,0	1.0	150	T <sub>deq</sub> ,°C↓ phr/phr	T <sub>deq</sub> ,°C↓ phr/phr	T <sub>deq</sub> ,°C↓ phr/phr T <sub>d</sub>	phr/phr	phr/phr	phr/phr	phr/phr	T <sub>deq</sub> , °C↓				1.000	
		100					45/6	1.0	150						
		120						1.1	120						
		60				Sec. of			60						
		Outdoor conditions							Outdoor ∞nditions						
	0.8	150						0.8	150						
		120							120						
		60	1						60						
		Outdoor		-					Outdoor						
	0.6	donanions	-			~		0.6	conditions		-	-			
	0.0	100						0.6	150						
		120							120						
		60						1	60						
		Outdoor conditions						Outdoor conditions							
	0.4	150						0.4	150						
		120							120						
		60		[					60	-					
		Outdoor	-	100				1.1	Outdoor						
		conditions						· · · · ·	conditions				1		
	0.2	150								0.2	150				
		120							120			-			
		60	1						60						
-	Outdoor conditions			Outdoor conditions											
	0.0	150						0.0	150						
		120							120						
		60		•					60						
		Outdoor	-					(	Outdoor						

Figure 1. Visual appearance of formulations degraded at the indicated temperatures (150, 120 or, 60°C) or, at the environmental outdoor conditions, during the indicated normalized times (t\*); the used DEHP/ESO ratios and  $X_{CaSt2S}$  are indicated in figure.



Figure 2. Polyene concentrations before post-processing  $(P_n^{o})$ , polyene accumulation rates during the indicated postprocessing conditions  $(dP_n/dt)$  and, percentage decrements on polyene concentrations in the post-processing at environmental outdoor conditions  $(\Delta_{dec})$  for formulations prepared with the indicated  $X_{CaSt2}$ ; for samples degraded at environmental conditions, the  $dP_n/dt$  values indicated in plot must be divided for 24 to obtain the real value of the polyene accumulation rate.

Besides, for the three formulations considered in Figure 2, such percentage decrement increases as the *n* value decreases. After of the initial period (~15 days), all samples maintained their respective  $P_n$  values practically constant during certain fraction of the test, up to the characteristic  $t_{min}$  value;

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the  $t_{min}$  values can be observed in Table 1. After such stable period, all samples accumulated the different polyenes at a rate that was constant during the rest of the test that could be characterized. Due to the high absorbance of some samples (>2), the polyene concentrations can only be measured during a fraction of the degradation test; for each formulation, the degradation time corresponding to the last characterized sample ( $t_{ult}$ ) is presented in Table 1, and the corresponding accumulation rates are plotted in Figure 2. There, it can be noticed that, the accumulation rates are strongly determined by the degradation temperature, showing a direct relationship between the dP<sub>n</sub>/dt values and such temperature. However, the accelerating factors that characterize the temperature effect are clearly dependant on both, the *n* value and the formulation composition; additional details about temperature effect are not presented here, but, they will be exposed during interactive presentation.

DEHP/ESO, phr/phr	X <sub>CaSt2</sub>	t <sub>min</sub> , h	t <sub>ult</sub> , h
	0.0	3240	3648
45/6	0.2	3648	3984
	0.4	3240	4368

Table 1. Characteristic time values (t<sub>min</sub> and, t<sub>ult</sub>) for indicated formulations degraded at environmental conditions

# Conclusions

The polyene accumulation behavior and the color changes produced on a set of formulations isothermically heated or exposed to environmental conditions were presented, demonstrating that, the trends observed at a given degradation temperature, usually can not be extrapoled to another temperature values. Besides, the samples degraded at environmental conditions shown distinctive behaviors as compared with the ones observed on isothermal heating. Therefore, adequate scaling factors for the polyene accumulation behavior can not be proposed, making difficult the application of the trends observed on accelerated experiments, to the prediction of the behavior at service conditions.

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# DESIGN OF SMART ASPHALTS FOR DETECTING STRUCTURAL DAMAGE

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#### 1. Abstract.

Rapid deterioration of asphalt roads due to environmental conditions such as temperature, humidity, UV degradation, etc, and those related to load situation such as statics, dynamics and shear stresses have obliged to improve the employed materials by developing new techniques that allow the obtaining of more resistant pavements. Incorporation of conducting fillers to an asphaltic matrix provides the possibility for monitoring in situ and in real time the initiation, propagation and fracture development on an asphaltic surface through the observed change in electric conductivity. Additionally, the incorporation of an elastomeric component to the asphaltic matrix, essentially viscoelastic, would improve the elastic behavior notably. In this work a pavement with improved mechanical properties is being developed, at the same time, this asphalt is going to be modified in order to obtain a smart material that can be used as a sensor capable of monitoring its performance during its application by sensing the fracture process due to environmental factors and load stresses.

#### 2. Introduction.

Many roads are made around the world and a lot of them are asphalt-based composites. Used tires are a very big problem around the world, only a small percentage of them are recycled, but the chemistry process to recover them produces pollution, instead of this the physical recovering is a clean procedure and it is possible to make aggregates that can be used in asphalt-based composites. The construction companies usually used mineral aggregates mixed with asphaltic products to build pavements structures. It is necessary a lot of energy to extract mineral aggregates, it is a dangerous procedure and pollution is generated, moreover extraction places are used as garbage deposits. This research proposes the use of aggregates made with disposal tires to make an asphaltic-based composite material; it was a mixture that combines an asphaltic emulsion and tire recovering aggregates. By other hand, all civil infrastructures around the world are suffering damages due to heavy load transit, UV rays, and so on. The world trend to detect damages and prevent failures is monitoring structures. To convert an asphaltic-based material in a intrinsic sensor, is necessary to increase the electrical conductivity. Some studies have experimented with different types of conductor materials into the mixture as: carbon fibers, graphite, and so on. The piezoresistivy has been studied in conductive asphaltic concrete by Liu and Wu [1] with different of loads arrangements for tension, compression.

## 3. Experimental procedures.

A composite material was made using particles from disposal tires; asphaltic emulsions and steel conductive particles. Two mixtures were made: 1) a non electrical conductive mixture; and 2) a conductive mixture using steel particles. The tire particles were obtained from a factory

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which rehabilitates tires and produces a lot of disposal tire particles; these usually go to garbage places. All tire particles passed the # 10 sieve. Three types of asphaltic emulsion were used: 1) Superstable (SE); 2) Fast Breaking No. 60 (F60); 3) Fast breaking No. 65 (F65). Steel conductive particles were obtained from a steel workshop as a disposal material. No water was used in the mixtures.

Tires particles mass was the main reference to design mixtures. Mixtures were made with different percentages of asphaltic emulsion: 10 %, 30 % and 60% respecting to tires mass. Steel particles were: 20 %, 40 % and 60 % of tires mass. Cube specimens of  $2 \ge 2$  inches were made. Table 1 shows different mixtures.

Tuene III Ispin		in thes purchases	
Туре	Tire particles	Emulsion	Steel particles
Emulsion	(g)	(g)	(g)
SE	50	25	
F60	50	25	
F65	50	25	
SE	15%	25%	60%

 Table 1. Asphaltic mixtures with tires particles and steel

Metal molds were used to make cubic specimens of two inches. A universal machine SHIMADZU of 100 kN was used to load specimens. Digital balances were used to determine mass. Digital tools to measure geometrical characteristics. A FLUKE multimeter 189 was used to measure electrical resistance; it was connected to computer by an infrared connection and software was used to capture resistance each second.

Two mixtures were prepared: 1) without conductive particles and 2) with conductive particles. Six cubic specimens were prepared for each combination. A compression test was used to get elastic modulus and ultimate stress.

To study the electromechanical coupling, a specimen was prepared with two opposite sides with silver paint and two connected wires. The electrical resistance was measured for 5 minutes to get Ro which is the condition without load. Afterwards the specimen was subjected to compression load to 5 mm/min and electrical resistance was measured at the same time each second, a preload was made before the final load to prepare the specimen. The specimen was tested until failure.

#### 4. Results.

The conductive property of asphalt-based composite depends on its microstructure. Because steel particles mix would modify asphalt mixture. When the conductivity of dispersed component is far higher than that of matrix material, it changes along S shape curve between the conductivity of asphalt and the content of dispersed component. When the volume fraction of dispersed materials is lower than certain critical value, the conductivity of asphalt concrete changes little with dispersed component increasing, but when the volume fraction of dispersed materials reaches the critical value, the effective conductivity of asphalt concrete will change abruptly. After that, once again the conductivity remains little change as the dispersed material increases. This is called a percolation phenomenon [1] and it is occurred in asphalts as well.

Figure 1 shows the compression strength-strain curves for four specimens without steel particles. The elastic modulus average was 0.78 MPa. The lineal behavior finishes at 0.48 MPa as an average. The Figure 2 shows a compression strength-strain curve of the specimen with steel particles, the elastic modulus is 1.6 MPa which is the double of mixtures without steel particles.



Figure1. Compression strength-strain curve of specimens without metal particles.

Electrical conductivity of specimen with 60% of steel particles was  $1.96 \times 10^{-8}$  S/m which it is between glass and silicon and into the semiconductor materials; the volumetric resistivity was  $5.11 \times 10^{7}$  ohm cm. A threshold value was reported [2] for volumetric resistivity as  $10^{-10}$ ohm cm for a 11% in that mixture. Similar electrical conductivity values of this study with reported [2] for mixtures within 10-13% graphite in asphalt-based composites as  $4.4 \times 10^{-9}$  and  $6.7 \times 10^{-6}$  S/cm. Another study [3] reported an increase in the electrical resistivity by adding conductor fibers from to 5.86 to 8.76 % resulting  $82.5 \times 10^{-2}$  to 420 ohm m.



Figure 2. Compression strength and strain of a specimen with steel particles

Figure 3 shows the resistance R of samples was measured as a function of the applied compressive stress amplitude. A uniaxial pressure was applied to electrical conductive asphalt and the resistance changed under the stress. This effect is named piezoresistance in conductive composites. The coefficient of piezoresistance  $\rho$  is usually calculated using the equation 1:

$$\rho = \frac{R_{\sigma} - R_0}{R_0 \sigma} \tag{1}$$

Where  $R_0$  and  $R_{\sigma}$  are the resistances of the samples uncompressed and compressed at the  $\sigma$  level, respectively. The value of  $\rho$  is higher, the sensitivity of piezoresistivity is better. The strain responds to the compressive stress, and the coefficient of strain sensitivity is given by:

$$k = \frac{R_{\varepsilon} - R_0}{R_0 \varepsilon} \tag{2}$$

Where  $R_{\varepsilon}$  is the resistance measured at  $\varepsilon$  strain.

The first zone shows a non-compression load which shows an electrical resistance with small variation; the first decrease forming a peak was due to a pre-load; a second zone was another constant electrical resistance without load; the final compression load was at 300 seconds, when the load began the electrical resistance decreases as an inversely proportional relationship. When the load stayed constant the electrical resistance was stayed too. Afterwards, the load decreased and the electrical resistance increased. There is a correlation ship between compression load and electrical resistance. A study [2] reported an electrical decrease when asphaltic material is subjected to compression load.



Figure 3. Electrical resistance developed with a compression pre-load and load.

Figure 4 shows the fractional changes in resistance  $\Delta R/R$  and strain  $\Delta l/l_0$  during the compressive loading for conductive asphalt. During the beginning loading, DR/R decreased rapidly. After the beginning loading process, DR/R changed little when the specimen was compressed. Finally the resistance is increased with the specimen was destructed gradually.



**Figure 4.** Fractional changes in resistance  $\Delta R/R$  and longitudinal strain  $\Delta l/l_0$ 

# 5. Conclusions.

Conductive asphalt is analyzed in this paper. A conductive path may exist in the steel powders because there are randomly distributed in the asphalt emulsion. Experimental results demonstrate that the stress has a great influence on the resistance of conductive asphalt, which exhibits sensitive piezoresistivity.

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# POLYMERIC SENSOR FOR DETECTION OF AQUEOUS SOLUTION.

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# Abstract

The research center in advanced materials in its area of polymers has been working for over a decade in the development of polymeric sensors and very specifically in distributed sensors, an example of this development is the ability of polymeric sensor for detection of aqueous solutions, this types of sensors have the characteristic of an event not only detect but also locate the event, this feature is utilized to monitor large and complex installations where the goal of sensor installation is to locate leaks, since the time of the location a leak becomes of great importance, due to damage or loss that they can cause, it is noteworthy that these functional prototype development

are therefore are multidisciplinary developments and intervening areas of knowledge such as chemical synthesis, plastics processing, signal processing and software development, all to achieve the desired objectives.

# Introduction

One of the areas within the applications of sensors, sensors are distributed, they are distinguished by the fact not only to detect an event for which they were designed, but also to locate the event within the vicinity of the installation of distributed sensor, such as: humidity sensors, pH, hydrocarbons, presence of gases, water, etc., would be expected in the development of distributed sensors, faces a greater challenge than developing specific sensors, this by the contain features fact that the sensor must that allow both sensing an event. and to differentiate the occurrence of the event according to the position where it appears with respect to the installation of the sensor, one of the performances of such sensors is as cables, as this is lengths to accomplished great cover. but it is necessary that the material which comprises actuating the sensor is exposed to various conditions that may be adverse to the different types of materials which are manufactured as sensors are ceramic, semiconductor, etc., but piezoelectric. not certain group of polymers that can be exposed to inclement weather and other external factors, all this gives rise to the development Inca distributed sensor polymers, because if the material is a plastic acting, this could be extruded and generate leads that support various operating conditions.

In CIMAV have developed various sensors distributed polymer, focused on solving demands of various industrial sectors such as: polymer sensors for the detection of aqueous solutions.

# 1. Polymeric Sensor for Detection of Aqueous Solutions

The objective of development of this sensor is to provide constant monitoring service to detect spills and leaks of water in aqueous solutions.

This system has an amphiphilic polymer acting part, which contains salts of lithium, copper and nickel - chromium and a winding coil, the operation of this sensor is that when water comes in contact with the sensor, it swells, its amphiphilic character and releases lithium salts, which dissolve and create an electrolyte, which together with metal wires, creating abridge electrolyte generates a current in the system, an issue that is used to sense and locate the event, the detection is attributed to the increase of current in the system and the location through an analysis of an equivalent electrical diagram node, hence the value of nickel wire like, which has a value resistance by length, of considerable size and its homogeneity in this parameter over the cable, the component parts of the sensor is shown in Figure 1.



Figure 1. - illustration of the water sensor.

# 1.1 Method of detection and localization

Applying Ohm's law (1) and resistivity equation (2), obtained in the equivalent circuit analysis (Figure 2) the location of a bridge created by the presence of water in the sensor and the detection is shown in equation (3).

$$V = I * R (1)$$

$$R = \rho * \frac{L}{A_{r}} (2)$$

$$L_{1} = \left[ \frac{I_{2} * (L_{T} * \rho / A_{T} + B)}{(I_{1} + I_{2})} - B \right] * \frac{A_{T}}{\rho} (3)$$



### Experimental

During the preparation of the pre-emulsion care should be taken in the addition of reagents, as we can affect the polymer, and the time to add the burden of initiators, it must be very careful in how you added and the time required for this, since it can be one of the factors by which the polymer can flocculate to avoid this is to comply strictly with the times stated above.

Another factor to consider is the design, which at first included the Triton X-305, which was changed by the Triton X-405, due to changes that occurred in developing the ter-polymer was decided to use Triton X-405 for the colloidal stability that this required, and therefore, the emulsion polymerization proved to be an effective technique for the scaling process, which gave us a 40% solids and 95% average conversion.

#### Flow diagram of the characterization of the polymer

Polymerizations were carried out to achieve various amphiphilic polymers with the characteristics of absorbing and drying need to run as fast as possible and at the same time the event occurred first condition can recover, a craftsman polymerization process described in the following diagram continuation flow figure 3.



# **Results and Discussions**

The ideal characteristic behavior of the sensor have shown in fig 4. Represented on the ordinate the intensity of electrical current (A) and the axis of the abscissa the time. As the polymer comes into contact with an aqueous solution, it grows as a function of time, this gives guideline to know that the longer it is exposed to an aqueous solution have a greater degree of precision in our calculations to give the location of event.



Figure4. Characteristic behavior of the sensor subjected to water absorption

## Conclusions

With the completion of this project could achieve a polymeric sensor for the detection of aqueous solutions, which has the ability to be distributed, which will give the exact location of the event, while the quality has to locate several events once it removes the liquid polymer absorbed. With this adjustment the sensor has the ability to recover thereby improves the utilization of this technology as if it were not so distributed sensor in each event would have to be changed in order to locate the different events.

In the synthesis must be cared quantities, times, temperatures, order of addition and this is able to obtain the desired parameters for the scaling of the sensor, resulting in a sensor cable can be processed in hundreds of meters.

#### Acknowledgments

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# COMPUTER SIMULATION OF FILAMENT ETHYLENE VINYL ACETATE (EVA).

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# Abstract

Computer simulation today is a reliable tool that enables process optimization. For this investigation are useful because they are powerful at simulation of fiber optic vibrations and temperature changes, the simulation was referred to EVA polymer in question at various mechanical and different temperature gradients. This is to know the strength of the polymer on these conditions and be able to make the polymer as a coating for optical fiber without it to lose its sensitivity, and their properties.

# Introduction

# Polymer used: Ethylenvinylacetate - (CH2-CH2) n-(CH2-CHOCOCH3) m-

The generation of 3D geometry was performed with SolidWorks software support, then we imported to the virtual laboratory. In which the mesh geometries, as required, including the physical printing on the desired study. To obtain these results, we applied the use of COMSOL software as virtual laboratory. [5] As a result of shear stresses in the fiber produced by the actions or stimulated that we achieve to detect. The foster the presence of these stimuli given the task of testing that would allow the development of geometry in the fiber optic carrier able to:

- ✓ Maximize the presence of harmonic mechanical actions, such as acoustic signals.
- ✓ Minimize the actions of stress.
- ✓ Maximize the exposure of the fiber to a temperature gradient [4]

# **Experimental vibration.**

Three of the geometries are shown below, with respect to the straight section extruded to the bearer of the optical fiber, which were called because its shape, "circular", "H" and "Y". In all cases, consider the location of the optical fiber eccentric circular region, the "H" has the ability to carry four fibers and finally the geometry "and" carries three optical fibers, using the model of "Solid Mechanics".



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Below are three of the geometries, with respect to the straight section extruded to the bearer of the optical fiber. Figure 1. Geometries considered a) Cylindrical geometry mesh, b) Geometry "Y", c) Geometry "Y" helix, d) geometry "H", e) geometry "H" helix.

In these cases we consider:

- ✓ The extruded sections of constant area, in order to prove how much energy is required to facilitate the displacement of 0.5mm at the center of a 50 cm segment of our carrier.
- ✓ Looking closely at the geometry "H", is identified by basic principles of mechanics, double action camber or simple camber to oscillate in the vertical (<sup>↑</sup> H) or horizontal (↔ H) to form "H". As I consider this variant, and simulate their response.
- $\checkmark$  We tested the action of cutting forces, subject to a double bend.
- ✓ It also was considered for the geometries "H" and "Y", the extruded helical, based on initial results and simulated tests. In order to promote the action of cutting forces.
- ✓ The extruded to all previous cases with constant radius, taking as base the radial position of the optical fiber, in order to contrast the above results.

# Table of number of nodes and elements in the mesh.

NUMERICAL MODEL	STRESS ANALYSIS Type of elements : Tetrahedron Distance between nodes (polymer): 0.0020 a 0.0275 [m] Distance between nodes (fibra óptica): 0.005 a 0.04 [m]				
Geometry	Number of Nodes	Number of Elements			
Cylindrical	3.798	1.473			
Y lineal	144,837	27,725			
Y helix	147,261	28,992			
H lineal	245,793	41,783			
H helix	233,223	39,169			
Optical fibre	80,322	14,604			

# Experimental data for temperature simulation

Experimental data for temperature simulation						
Composite	units	EVA 460	SOIL			
Density	Kg/m3	rho(T)	5.515			
Thermal Conductivity	W/(m*k)	0.31	K(T)			
Ср	J/(kg*k)	125.8	C(T)			
Poisson Coefficient		0.37				

This work in 2 dimensions, we simulate the temperature and heat transfer from the sensor in an area of soil.

- Module is used for heat transfer in solids.
- Applying a low temperature of 273°k and high 303 k at the ends of the geometry to visualize the change that is when it passes the sensor geometry, so we can see which of the three geometries is the best in temperature, and decide how best to produce the sensor.

It take a time of 70 seconds, the simulation can be seen from the following images where taken into account the time according to the change that appeared in each of the geometries

# **Results and Discussions**

Vibration and stress.

The simulation results shown demonstrate the presence of shear, even though they provide different scale efforts along the fiber. It is of interest to magnify this response, associated with the stimulus of stress, temperature or acoustic. [3]. The result of this simulation give us guidelines to consider give the wearer a spiral effect, with two intentions, to maximize the effect of these shear efforts and minimize stress. The second reason has to consider that the optical fiber is a material that does not tolerate axial strain. So the design must absorb this effect, without generating the action of elongation of the fiber, for which the geometry test "H" and "Y" helix effect. First for the case of a bending action generated by the elevation of 5 mm at the center of a length of 50 cm, which was previously made for the extruded linear.



Figure 2. Efforts Mises surface fiber optic carrier, in a simple linear extruded, considering the variation in geometry "H" on its horizontal and vertical deformation.



Figure 3. Efforts Mises carrier surface of fiber optics, geometry, "Y" and "H" in an extruded helical.



Figure 4. Effect of stretching, 1 [cm] "H" and "Y" helix. Shear, the vectors are not constant in magnitude and exhibit a change in direction.

The following table it s the summarize the results for this test are presented above, and it indicates the result of considering a constant area in its cross section (38.95 mm2),

Straight Section	on cte. 38.95 [mm2] 0.5 m	m prescribed displacemer	nt, 0.5 m long
Geometry	Max effort. [10 <sup>5</sup> Pa]	Von Mises Vol Energy	E. volumetric
		[J]	displacement
			[10 <sup>-4</sup> J]
Cylindrical	0.961	0.373	1.228
H lineal	1.553	0.637	4.077
Y lineal	1.173	0.419	1.696
H helix	1.873	0.667	4.219
Y helix	1.183	0.426	1.687

RADIO cte.	3.5 [mm] 0.5 mn	n prescribed displacement, 0.	5 m long
Geometry	Max effort. [10 <sup>5</sup> Pa]	Von Mises Vol Energy [J]	E. volumetric displacement [10 <sup>-4</sup> J]
Cylindrical	3.798	1.473	4.853
H lineal	1.065	0.437	2.797
Y lineal	1.173	0.419	1.696
H helix	1.284	0.457	2.894
Y helix	1.183	0.426	1.686

Harmonic mechanical actions: helical geometry is tested in "H" and "Y", not only by action of a static deformation, we show how to amplify the action of shear stresses under a harmonic stimulus.

Deformation by elongation: for this situation test is limited to helical geometries, since the extruded line so do not provide tolerance to fiber optics for this deformation, causing catastrophic damage. This damage may arise in the installation of the field, during handling to exceed the breaking strength of the fiber. To consider this case, the carrier is simulated with extreme deformation of 2%, the segment of length 0.5 m, is stretched in 1 cm.

Stress experienced by Eva 2% Elongation			
Geometry	No. Nodes		
"Y" Helicoidal	3.044		
"H" Helicoidal	2.529		

The summary of the calculated maximum efforts in the LV is shown in the table below,

Breaking stress Fiber Optics: 960 [106Pa], exceeding showing Eva effort as a means of support, in its turn to be deformed by 2% of its length.

# Temperature.

The EVA-coated optical fiber was subjected to an environment, which was within an area of common ground, a distance of 50 centimeters of soil, in order to submit it to a temperature gradient which was at room temperature 310°K and we applied cold temperatures to determine the distance 273.15°k ideal to which must be placed and coated optical fibers to detect the temperature change.

# Conclusions

From the evidence in LV, it is concluded that the appropriate geometry to be used as the carrier of the optical fiber geometry is "Y" helix able to:

- ✓ Maximize the presence of harmonic mechanical actions, such as acoustic signals, Possessing a lower energy value to achieve their displacement: 1,687 [10-4 J]
- ✓ Minimize the actions of stress present, without it being able to avoid detection. When considering an extreme elongation of 2%, the maximum stress of 3044 MPa, while the breaking strength of the optical fiber is about 960 MPa.
- ✓ Maximize the exposure of the fiber to a thermal gradient, geometry provides exposure about 80% of its surface, in a stimulus face.
- ✓ Finally, the system considers the management of three separate radiation, and therefore must be guaranteed equal opportunity to receive the carrier stimulus, this is also achieved through the helical arrangement.
- ✓ With respect to the experimentation that took place in the simulation of temperature was found that EVA polymer in question is capable of detecting a temperature change in the conditions mentioned above in a time of 10 to 20 seconds the polymer takes the cold temperature she underwent. This prove that the polymer is sensitive to temperature so it will not affect the sensitivity of the optical fiber.

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# OPTIMIZATION OF EXTRUSION PROCESSING CONDITIONS OF BLENDS WITH RECYCLED HDPE AND PINE RESIDUES: PRELIMINARY STUDY BY CAPILLARY RHEOMETRY

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The use of recycled plastics and vegetal residues (e.g., HDPE and pine wood) to fabricate alternative materials are a good option de lower uncontrolled generation of urban waste. It has been reported that extrusion is widely used to obtain such materials, and the importance to optimize processing conditions taking into account blends' composition and interaction between raw materials and additives, among many other factors [1]. In this work we report on the processing of blends of recycled HDPE and pine residues (PR) by using a single-screw extruder, which was employed to estimate the apparent viscosity by capillary rheometry as a tool to find out the most favorable processing conditions to obtain the materials with optimal mechanical properties. A coupling agent and a processing aid were used as additives. Preliminary results indicate that the blends' viscosity was affected mainly by the content of PR. In the same way, the processing aid increases the extruder output. However, contradictorily, it promotes degradation of PR. It was also observed an erratic behavior of pressure vs. time during blends' extrusion, which can be attributed to poor dispersion of PR particles within the HDPE. This phenomenon has also been reported in other works [2].

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[2].Burlett D.J., *J. Therm. Anal. Cal.* 75, 531–544 (2004).
# APLICATION OF POLYMER RHEOLOGY TO WHEAT KERNEL AND THE RELATION TO SEDIMENTATION VOLUME AND MIXING TIME

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Within the cereals industry there has been a long history of using descriptive empirical measurements of rheological properties, with an impressive array of ingenious devices such as the Amylograph, Farinograph, Mixograph, Extensigraph, Alveograph, various flow viscometers and fermentation recording devices, among others [1] The reaction force and stress-time history was used to describe the viscoelastic behavior of the wheat kernels under the application of constant strain or deformation [2].

In the present work we shall, first, briefly describe those stress relaxation conditions of wheat kernels; next, and important, we discuss the comparative results of quality traditional characterisations of thirty six lines of bread wheat, which contain varying high molecular weight-and low molecular weight-glutenin subunits. These investigations include SDS-sedimentation volume and long mixing time, among others.

Finally, we present correlation between relaxation time and mixing time and SDS sedimentation volume results that may increase the efficiency of grain selection for processing, marketing and end use.

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# MEASUIRING THE SURFACE TENSION OF A DROP BY USING AN EVOLUTIONARY ALGORITHM

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We present a numerical method for measuring the surface tension of a drop. Polymer drops were analyzed in optical compared with precision of  $1.0 \,\mu\text{m}$ , which is an excellent means of measuring small objects and complicated geometry through the display of the magnified image on a translucent screen. We find the profile related with the analyzed drop by transforming of fitting a polynomial into an optimization problem, which is then solved using an evolutionary algorithm. Our numerical results show that our method yields a more accurate solution that other methods commonly used to solve this problem.

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# ENZYMATIC DEGRADATION OF POLYURETHANE/CELLULOSE DERIVATIVES-POLYACRYLIC ACID

2

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## Abstract

This study examined the effect of protease on the degradation of castor oil, 2,4-tolylene diisocyanate (2,4 TDI), cellulose acetate, and hydroxiethyl cellulose, based polyurethane (PU) polyacrylic acid (PAA) sequential interpenetrating polymer networks (IPNs) were synthesized. PUs were prepared by reaction of hydroxyl groups from castor oil, and cellulose acetate or hydroxyethyl cellulose with 2,4 TDI, using dibutyl tin dilaurate (DBDTL) as catalyst. PUs were swollen in acrylic acid monomer solution and subsequently polymerized by radical polymerization initiated with 4,4-azobis(4-cyanovaleric acid) (ACVA), and N,N'-methylenebis acrylamide (NNMBA) as crosslinking agent. Series of three PU/PAA ratios (75/25, 50/50, 25/75) were prepared. Treated polyurethane films were characterized with SEM, attenuated total reflectance Fourier transform infrared (ATR-FTIR). The polyurethane films were removed from the treatment solution and vacuum dried for 24h prior to analysis. IPNs films were incubated in a buffer control for 15 days. The study confirmed than enzymatic degradation, is responsible for the observed biodegradation of IPNs. Signal of the carbonyl group of the PU due to the catalytic action of enzyme in the three relations of the IPN. The variation of the area of this band appeared in amplitude and height. The IPNs films showed a decrease of the band of the carbonyl group characteristic peak of the base polyurethane due to the enzymatic action for the three synthesized relations of the IPNs. The morphology of two phases was studied by SEM. A brightness loss and a phase separation appeared when the PAA content was increased. For three PU/PAA ratios, for a 75/25 relation, the sample reveals layers or fractures, and a phase separation between them.

# Introduction

An interpenetrating polymer network is a material containing two (or more) polymer networks, which are combined and at least one of them is synthesized and/or crosslinked in the immediate presence of the other. Crosslinked polymer networks are held together by permanent entanglements with only accidental covalent bonds between the polymers. The three conditions for eligibility of an IPN are: (1) the two polymers are synthesized and/or crosslinked in the presence of the other, (2) the two polymers have similar kinetics, and (3) the two polymers are not dramatically phase separated.

IPNs offer the possibility of combining in network form which otherwise are non-compatible polymers with opposite properties (Pissis *et al.*, 2002; Sperling 1981). As long as the reacting components are mixed well during synthesis, thermodynamic incompatibility can be overcome due to permanent interlocking of network segments and IPNs with limited phase separation are obtained (Hsieh *et al.*, 1999).

Polyurethanes comprise a kind of materials that can vary from rubbery to glassy thermoplastics from linear polymers to thermoset. This versatility can be further controlled in terms of processing and composition to fulfill a vast variety of product requirements (Hsieh *et al.*, 1999). The IPNs formation, be either by "sequential" or "simultaneous" network formation, has often brought about remarkable synergism in properties such as mechanical, thermal, and energy absorption (Parizel *et al.*, 1994).

Cellulose has been re-evaluated as a functional material to meet diverse needs of today's society as a result of the unique reactivity, biodegradable, biocompatible, hydrophilic, and chiral characteristics (Zhang *et al.*, 1999). Abundant hydroxyl groups in cellulose derivatives facilitate the formation of polyurethane groups with isocyanate groups from 2, 4 TDI. PU based on cellulose derivatives were prepared and tested for biodegradability (Rivera *et al.*, 2002). Morphology and properties of IPN's depend upon the degree of phase morphology, which is related mainly to polymer miscibility. The goal is to interpenetrate networks when IPN's are made of immiscible components (Vlad *et al.*, 2002).

The degradation studies were realized using enzymatic hydrolysis, under controlled conditions of pH and temperature. Under these conditions it was determined the degradation of the IPNs by FTIR.

# Experimental

# Materials

Castor oil with density 0.961g/mL at 25°C; 2,4-tolylene diisocyanate (2,4-TDI), 95% purity, 74.16g/mol molecular weight and 1.214g/mL density at 25° C, and dibutyltin dilaurate (DBTL), 95% purity, density 1.066g/mL at 25°C were used for the synthesis, all were purchased from Aldrich. Cellulose acetate (CA) MW ~30,000, 1.3 g/mL density at 25°C and 2-hydroxyethyl cellulose (2-HEC), MW ~250,000, 0.6 g/mL density at 25°C, also from Aldrich. The acrylic acid (AA), purity  $\geq$ 99.0% (GC), 1.051 g/mL density at 25° C were also from Aldrich. 4,4-azobis(4-cyanovaleric acid) (ACVA), 98% purity, 280.28g/mol molecular weight was from Fluka. The N,N'-methylene bisacrylamide (NNMBA), 98% purity, 154.17g/mol molecular weight from Aldrich was used as crosslinker. 99.9 % purity ;acetone from Fermont was used as solvent. All reagents were used as they were received from suppliers.

# **Polymer synthesis**

The IPN's were synthesized by sequential method. PU synthesis was carried out adding castor oil, cellulose derivatives and 2,4-TDI to the reactor previously mixed at room temperature. Acrylic acid was heated at 60°C, followed by crosslinnking agent addition. Afterwards, the acrylic acid solution was added to PU-prepolymer and mixed for 20 minutes. Stechiometric amount of initiator to acrylic acid was added at this stage and continuing heating to initiate polymerization. Finally PU catalyst was added to the reaction mix. After 20 minutes the prepolymers were moulded and heated for 24h at 60°C. IPN's were demolded and postcured for the next 24h at 60°C in a vacuum atmosphere (Hourston *et al.*, 1998, Cai *et al.*, 2000).

Isocyanate/castor oil + Cellu-lose derivative;		PU/PAA	
[NCO]/[OH] = 1.07	(% wt)		
Cellulose derivative (1, 3 % wt in PU)	75/25	50/50	25/75

Fable 1. Cellulose	derivatives	[NCO]/[OH],	(AC, HEC)
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## **Results and Discussion**

All the samples after being incubated by 15 days with enzymes under conditions of pH and controlled temperatures were analyzed by FTIR. In order to measure the variations of the absorption bands of the functional groups that are susceptible to the enzymatic attack.

The polyurethane films were removed from the treatment solution and vacuum dried for 24 h prior to analysis. Characteristic ATR-FTIR spectra of PEU films incubated for 15 days showed that the films incubated in papaine retained all characteristic bands.

The results are shown in figures 1, 2. The degradation of these IPNs were compared with their standards without treatment. In these results it is possible to observe the band of the carbonyl group at  $\sim 1,732$  cm<sup>-1</sup>.



**Figure 1.** FTIR spectra of IPNs with 3wt% CA - 2.5% ACVA, 1.5% NNMBA, treated in urease and papaine solution for 15 days at 37 °C



**Figure 2.** FTIR spectra of IPNs with 3w% HEC - 2.5% ACVA, 1.5% NNMBA, treated in urease and papaine solution for 15 days at 37 °C

Quantification of the changes in the ATR-FTIR spectra of specimens was accomplished by measuring peak heights using local baselines. Previous studies of poly(ether urethane) degradation have demonstrated a correlation between biodegradation and the loss of ether, methylene and urethane peak heights (Christenson, et al., 2006).

CA (3%)	Degradation (%)	HEC 3%	Degradation (%)
2.5 – 1.5		2.5 – 1.5	
75/25	18.8	75/25	7.8
50/50	18.9	50/50	6.8
25/75	13.2	25/75	4.7
2.5 - 2.5		2.5 - 2.5	
75/25	2.3	75/25	3.7
50/50	2.3	50/50	4.3
25/75	8.3	25/75	3.6

Table 1. PU/PAA system from ATR-FTIR peak height analysis. Papaine

Table 2. PU/PAA system from ATR-FTIR peak height analysis. Urease

CA(3%)	Degradation (%)	HEC (3%)	Degradation (%)
2.5 – 1.5		2.5 – 1.5	
75/25	11.6	75/25	19.8
50/50	11.8	50/50	7
25/75	17.8	25/75	1.7
2.5 - 2.5		2.5 - 2.5	
75/25	14.6	75/25	3.5
50/50	1.8	50/50	7.
25/75	11.2	25/75	2.8

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# Conclusions

It was possible to prepare IPNs PU based in castor oil CA and HEC/PAA, varying the crosslinker agent concentration, catalyst and PU/PAA ratio in 3 levels.

By FTIR was possible to detect characteristic signals of PU, PAA, but was not clear to prove presence of CA and HEC due to overlapping with other groups in the same typical region and because the cellulose derivatives amount was low.

Furthermore, there was no evidence of secondary reactions in PU and PAA network formation.

The degradation by urease and papaine enzymes is possible, although with moderate percentage.

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# MULTI-WELL ELECTRICAL CELL CULTURE

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## Abstract

A well electrical cell culture was designed and fabricated. The device was made in planar shape with acrylic material with five electrode-sensors. The growth zone submerged in a physiological fluid and the device's temperature was always controlled [1]. A switching circuit simultaneously connects the five electrodes, upon input of a DC power source or pulsed AC source, as required. Measured mapping of electrical field, and protocol standards were developed in order to assure healthy cells, avoid system-contamination and achieve optimal well-performance for cellular growth. The five electrode set were connected through internal ducts, so there was no contact with the physiological fluid [2].

Experiments have shown that a direct electrical current 250  $\mu$ A/mm2 on a Petri glass-dish, have no effects on the viability of cells cultured. The same is observed in experiments with insulating plastic plates at density current of 2.5  $\mu$ A/mm2 [3]. The device is adapted for use in an optical microscope

## Introduction

Notwithstanding that there are some studies on the effect of electric field applied to the cells it is possible to increase the performance of such devices. Cell culture studies provide valuable information cell's physiological condition and by extension the tissue and organism from which the cells originate. Among the many techniques that are currently available for cell culture monitoring, several information, such as cell adhesion, spreading and motility can be extracted from these techniques. The importance of the electrical control of cell physiology was becoming apparent from the famous experiments of Galvani [4]. Other research has found that the application of an Electric Field Stimulation (EFs) generates some specific electrochemical reactions, which contribute to the regeneration of living tissues [5]. In this work we discuss the design and fabrication of a well electrical cell culture in order to apply a DC electrical gradients of voltage within tissues (endogenous electrical fields), to study how cells respond to these gradients, and their role in development of the tissue repair.

## **Theoretical Discussion**

The Injury potential means as the potential difference observed between the injured and the noninjured regions of an injured tissue. An injury potential is a steady, long-lasting direct current (DC) voltage gradient induced within the extracellular and intracellular spaces by current flowing into and around an injured cell. It is known that the endogenous EFs are present for many hours or days at wounds and in areas of active cell growth and migration during development. So there is strong evidence that these are essential to regulate appropriate cell behaviors during tissue morphogenesis and regeneration [5]. To test the effect of electrical current on tissues, the gold-coated electrodes were assembled in the multi-well electrical culture plates. To effectively apply uniform EFs to a space within a well-defined boundary, such as within a tissue-regenerating scaffold, it is advantageous to use an organic biodegradable conductor as scaffolding materials. Previously, we have reported plasma polymerized polymers of pirrole, and presented as conductive surfaces [6]. A scaffold made of this material can be connected to an electrical circuit as a simple conductor whereby only the cells on or within the scaffold are affected by the EFs.

## Experimental

## **Device Design**

The design of the device consists basically of 5 units of cell culture and an observation point of cell growth, with optical microscopy. **Figure 1** shows the 5 electro-culture wells units arranged around a central cylinder, where wires that applied the direct voltage to each pair of electrodes in the well culture are joined. These wires also give back information on Injury potential (regenerative potential). This arrangement of 5 electro-culture wells is basically a cylindrical container with a heat bath which allows variation and temperature control. It has also a transparent cover with a cut section, which allows optical microscope observation and manual control allowing positioning a specific well of electro-culture under the optical microscope for observation.







For clarity, **Figure 2** (a) shows the position of silicon seals and (b) details of the deposit and the 5 well arrangements. By adapting two springs at each electrode we ensured good electrical contact. The silicon seals around the electrodes avoid electrical contact of the electrodes with the physiological fluid. **Figure 3** shows a perspective drawing of the electro-well and a cross-sectional view of this array. **Figure 4** represents the dimensions of the container with the 5 wells on an elevator support adapted to a microscope (Leika Dulp). In this figure, one can see the approaching of the window's well, in order to obtain the maximum amplification provided by this kind of optical microscope.



Finally it is expected that with this device we can achieve an effect of cellular growth like the showed schematically in **Figure 5**, and picture in **Figure**, [1]

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Figure 3



OPTICAL MICROSCOPE (Olimpus)



Figure 4

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Figure 5



Figure 6

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## Conclusions

We hope that our results and conclusions may give some light onto the validity of our system where the conductive polymer substrate is used as a simple conductor.[xx] There are also some specific questions related to the use of conductive polymers for EFs, like whether the conductive polymers might release dopant and residual chemicals during process, which may interfere with the effect of EFs.

This study addresses the role of EFs on the viability of human cell cultured on the PPy/PLLA composite membranes, clarifies the possibility of releasing cytotoxic products from the conductive membranes during EFs, and compares the impact of electrical field and current. The individual role of electrical field and current in EFs must be explored as well, which will shine light on future design of both materials and devices.

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# ADVANCED POLYMER MATERIALS: OPTOELECTRONICS AND MEMBRANES

# DEVELOPMENT OF MATERIALS FOR ORGANIC ELECTRONICS AND OPTOELECTRONICS

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Organic polymers with conjugation in the main chain or in pendant side groups have had a significant impact on a variety of organic electronic and opto-electronic applications. In this talk, I will highlight some recent advances in the synthesis and application of polymeric materials and methods to n- and p-dope such materials. Specifically, I will focus on the development of rylene diimide materials for transistor and organic photovoltaic applications and side-chain polymers that can be used for organic light emitting diodes.

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# AN INTEGRATED APPROACH FOR ENHANCING PERFORMANCE OF POLYMER SOLAR CELLS THROUGH MATERIAL, INTERFACIAL, AND DEVICE ENGINEERING

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An integrated approach combining materials design and synthesis, interfacial modifications, patterning and optical engineering, and device engineering have been adapted to develop low-cost, efficient and stable polymer solar cells. In this talk, we will discuss our recent development on polymer solar cells with inverted structure. Through the process optimization and interfacial modifications, inverted cells with power conversion efficiency of ~7% and improved ambient stability can be achieved.

We have implemented and characterized models for light propagation in polymer solar cell structures and coupled them to simulations of carrier dissociation and transport. These simulations were used to guide optimization of both standard and inverted device structures to maximize power conversion efficiency. Optical simulations have been used to determine optimum layer thicknesses to maximize optical generation in active device regions and thereby enhance short circuit current.

Finally, new synthetic methods to develop low-bandgap polymers with cross-conjugated structures and novel fullerene derivatives for efficient and thermally stable polymer solar cells will be presented. These new materials will be further studied based on our integrated engineering approaches to fully harness their best potentials as PV materials.

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## ELECTROPATTERNING AND COLLOIDAL TEMPLATING OF ULTRATHIN POLYMERS FILMS AND BRUSHES

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A facile approach and strategy towards binary composition, two-dimensional (2D) patterned surfaces of conducting polymer periodic arrays together with thiol self-assembled monolayers (SAM)s and electropolymerized macroinitiators is described. The method involved a Langmuir Blodgett (LB)-like deposition of latex microsphere particles, electropolymerization by cyclic voltammetric (CV) technique, and self-assembly of an amphiphile. The LB-like technique enabled the monolayer deposition of different sizes of polystyrene (PS) particles in hexagonal packing arrangement on planar substrates. Combining the LB-like method with CV electropolymerization is advantageous as it provides deposition control of a polymer interconnected network, controlled composition ratio of polymer and SAMs, and control of 2D size and spacing of the spherical void pattern.. The dual patterned surface provided a good imaging contrast as observed by atomic force microscopy (AFM). Complimentary analyses such as xray photoelectron spectroscopy (XPS), attenuated total internal reflection infrared (ATR IR), UV-Vis spectroscopy, and static contact angle measurements were used to characterize the formation of the patterned surface. The versatility of the method enables the potential for making various types of quantitative binary compositions and patterned surfaces using different combinations of conducting polymer or functional SAMs, which can be extended in the future to polymer brushes and layer-by-layer assembly of various materials.

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## NANOGELS AND NANOSTRUCTURED HYDROGELS

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Currently, hydrogels are encountered in drug and water-and-nutrient delivery systems, prothesis, superabsorbent sanitary towels and diapers, soft lenses, etc. In all these applications, the swelling capacity and the mechanical properties, particularly in the swollen state, play important roles. In fact, the combination of high swelling and improved mechanical properties are highly desirable. Here we report the synthesis of nanostructured hydrogels with higher water absorption capacity and better mechanical properties than conventional hydrogels. The nanostructured materials are made by a two-stage polymerization process: first, crosslinked nanogels or IPN's nanoparticles are synthesized by inverse microemulsion polymerization, dried and isolated. Then these nanoparticles are dispersed in an aqueous (or mixture of water and other hydrophilic solvent) containing a hydrophilic monomer(s) and polymerized to produce the nanostructured hydrogels. Several combinations of polymers in the first and second stages produce a variety of responses to changes in temperature, i.e., they are thermo-responsive, but most of them exhibit faster and larger swelling, larger de-swelling and superior material properties than conventional hydrogels made with the same polymer(s).

## POLYMER MEMBRANES FOR WATER PURIFICATION

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Polymer membranes will be critically important in addressing urgent global needs in the 21st century for reliable, sustainable, efficient access to clean energy and clean water. This presentation will focus on recent advances and applications of polymer membranes for water purification.

Polymer membrane-based desalination has been recognized as an energy efficient, low environmental impact route to produce clean water for a variety of applications. Additionally, ultrafiltration and microfiltration of aqueous streams have become important unit operations in many industries, including the water purification and wastewater purification industries. This presentation focuses on two new classes of polymers to attack critical problems in membrane-based water purification: (1) chlorine-tolerant desalination membranes and (2) fouling-resistant membrane nanolayers based on polydopamine.

Commercially available reverse osmosis membranes are prepared mainly from aromatic polyamides (PA). However, PA membranes suffer from poor resistance to continual exposure to oxidizing agents such as chlorine. Chlorine is the most widely used oxidizing biocide in water treatment because it is inexpensive and highly effective when present in water at levels of a few ppm. Disinfection of feed water to membrane desalination units is required to prevent biofilm growth on the membranes, which significantly degrades their performance. However, PA membranes cannot tolerate continuous exposure to water containing more than a few ppb of chlorine. This presentation discusses results from a systematic study of the desalination properties of a new family of highly chlorine tolerant, sulfonated polysulfones.1 These polymers are prepared via a novel synthesis involving direct copolymerization of non-sulfonated monomers with a disulfonated monomer. By controlling the content of disulfonated monomer in the final polymer, desalination properties, such as water permeability and salt rejection, can be varied over a wide range. A family of materials, based on random copolymers, phase-separated block copolymers, blends, and crosslinked materials may be prepared from these starting blocks to provide a new platform for desalination membranes.

Across many platforms of membranes, fouling mitigation is a major challenge to be addressed to achieve the most energy-efficient, cost-effective membrane filtration processes. Previously, many surface modifications and functionalized polymers were reported to prevent fouling. However, most of these techniques and materials are practically difficult to implement in water purification membranes. We have discovered surface treatment methodologies that can be used to prepare high permeability polymeric membranes from all common water purification membrane classes.2 These surface-modified membranes have persistent tolerance to fouling by proteins and emulsified oil, two ubiquitous contaminants in a variety of wastewaters. These membranes were prepared by depositing bio-inspired, self-polymerized hydrophilic polydopamine nanolayers on their surfaces. To demonstrate scalability of this modification, the nanolayers were also applied to entire membrane modules. Upon nanolayer deposition, the membranes could be further functionalized using fouling-resistant macromolecules, such as poly(ethylene glycol), to promote improved fouling resistance and, therefore, high membrane flux.

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# GAS TRANSPORT PROPERTIES OF MEMBRANES BASED ON NOVEL AROMATIC POLY (ARYLENEOXINDOLE)S

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To find generalized applications as gas separation means, polymer membranes must satisfy at least the following requirements: 1) to show commercially attractive combinations of gas selectivity and permeability properties, P(i)/P(j) - P(i); 2) to have high stability relative to the environment where they will perform and that it is determined by their thermal, volumetric, chemical and mechanical properties; and 3) to posses outstanding processing properties so they can be engineered as a hollow fiber or a flat sheet.

In this presentation, the efforts towards finding materials that meet some of the requirements will be presented and discussed in terms of the structure property relationship using the well-known protocol defined for a plot of selectivity vs. permeability. In particular, it will be shown how systematic changes in the polymer repeating units of 22 novel aromatic poly (aryleneoxindole)s have moved their P(i)/P(j)-P(i) combinations towards polymers that posses much higher permeability and selectivity. In fact, it will be shown it some of them fall close to the updated Robeson's "upper bound limits" for the separations of  $O_2/N_2$  and  $CO_2/CH_4$  and they compare well with the recently published fluorinated poly (ether imide) films containing phthalimidine moiety in the main chain [1].

In addition, it will be mentioned that the novel poly(aryleneoxindole)s, that posses moderate to high fractional free volume, high glass transition and decomposition temperatures and excellent chemical and mechanical resistances, have the added advantage of being easily synthesized, at room temperature, from relatively cheap monomers.

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# GAS TRANSPORT PROPERTIES IN POLYNORBORNENE DICARBOXIMIDES

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In this talk a review of several polynorborne dicarboximides with different pendant groups, that were synthesized by catalyzed ring opening metathesis polymerization is performed. The effect of the different pendant groups on the chemical, physical, mechanical and gas transport properties is discussed. It was found that phenyl pendant groups increase thermal properties as well as mechanical stability. It was also seen that substitution of triflourene groups in the pendant phenyl groups will increase gas permeation through the polynorborne dicarboximides which was attributed to an opennning of the structure, attested by a large fractional free volume. The increase in gas permeability coefficients in the polynorbornenes with pendant fluorine group substitutions was stable and did not change with time. Depending on the pendant substitution, these polynorbornene dicarboximide sustituted polymers present all the range of gas permeability and diffusivity options with reasonable thermal stability and mechanical properties.

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# MAIN CHAIN AZOPOLYESTERS I. THERMOTROPIC LIQUID CRYSTALLINE BEHAVIOR

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Liquid crystalline polymers (LCP's) are known as high performance materials for several optical and processing applications, which depend on their chemical groups and also the location of those groups into the polymeric chain [1]. Particularly, those LCP's containing azobenzene groups have attracted the interest in both the scientific and the technological fields because of the ability of this group for being trans-cis photo-isomerized by a laser beam [2]. In this work, main chain azopolyesters were synthesized through the polycondensation reaction of n-alkanedioyl dichlorides (n=6, 8, and 10) and azobenzene-functionalized diols containing two lateral m-alkoxy chains (m=6, 8, and 12). The thermotropic liquid crystalline properties of synthesized azopolyesters were investigated using polarizing optical microscopy (POM), differential scanning calorimetry, and Xray diffraction. By POM, a high fluidity typical Schlieren optical texture was observed indicating the presence of a nematic liquid crystalline (LC) phase, which was corroborated by X-ray patterns obtained at various temperatures. Results indicated that the mesophase stability and the clearing temperatures depend on the length of the lateral chains of the azobenzene derivative as well as the length of the flexible spacer in the main chain.

This work was supported by the CONACYT, México (Project 61773-R).

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# LIQUID HYDROCARBON POLYMER SENSOR

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## Abstract

The sensor is a patented formulation of polybutadiene, this has the property of swelling in the presence of liquid hydrocarbons, and the sensor has two windings nichrome wires distributed along the sensor coated with poly styrene-ethylene-butylene-styrene (SEBS). When the sensor makes contact with the hydrocarbon, the SEBS is dissolved and discovers the metals and besides the swelling of the body causes a short circuit. With a simple algorithm that uses the electrical resistivity of nichrome and ohm's law we obtain an equation that directly allows the location of the leak (Equation 1).

The present research summarizes the techniques of manufacture, physical properties of materials, user interface, mathematical methods, and presents laboratory results and field tests supported by graphic response with time and repeated testing (Figure 1).



Figure 1

## Introduction

The sensor manufacturing was performed by mixing various materials in a Brabender extruder, the final shape of the sensor is given by a dice shaper, after this process the sensor is heat treated at 175 Celsius degrees (cross linked) in a tunnel type oven to keep the final pattern, also the sensor has a central copper wire to reinforce this shape, the shape can only be changed by the interaction with any hydrocarbon, the following material needed list to manufacture the sensor body.

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## Components of the swelling polymer

- Polybutadiene (PB)
- 2 PHR stearic acid
- 4 PHR calcium stearate
- 4 PHR naphthenic oil
- 0.5 PHR carbón black
- 0.02 PHR dicumyl peroxide (DCP) as cross linking agent

The sensor has two current carrying wires needed for the necessary distance calculation of the leakage by the hydrocarbon contact at any point of the sensor, these wires are coated with SEBS, one of this is a bare copper wire, the other one is a nickel chromium alloy which offers linear resistance necessary for the reliability of the sensor, the coating method of these two wires is the same as the sensor body, the figure 2 shows the finished sensor.





The sensor body is black in color (3), the reinforcing wire is seeing in the center (1), the coated nichrome wire is a linear placed over the sensor (2) and it is sustained by the winding bare copper wire (4).

The signal fitness was performed by an own electronic card design, this is responsible for connecting the voltage to the lead wires and make a voltage divider with two  $22\Omega$  reference resistors, after this signal adjustment we continue with the data acquisition stage, it uses a National Instruments DAQ card (NI USB-6009).We used analog channels for voltage sensor acquiring and digital-type channels to drive the power relays outputs to trigger sirens and/or other signals to give notice of the event .

The continuous currents (DC) are difficult to break when a electric circuit is close or open, when we open a contact a spark jumps, sparks have a self-feeding process that allows them to grow, and that's continue involuntarily while the parts are in contact, so the spark grows in size, heat, and danger. The alternative current (AC) does not have this behavior, this can decrease the probability of spark to trigger a switch, at maximum one hundredth of a second after, the current becomes zero, so the spark is extinguished and cannot grow.

The manage voltage is 20 VAC to reduce the risk of spark and the contact of the wires is isolated due to the coating (SEBS), it is encapsulated to be dissolve at the hydrocarbon contact.

An interface was designed in Lab View software, the reason for using a high-level language is the ease of use that this software presents to the user, this provides four channels of detection, and a section where you enter a series of data obtained linear regression.

# Experimental

Before the construction of the sensor, we made a resistance test to nichrome wire reels to determine the linear resistance / length of this through a linear regression, it was used for this a bench meter by Agilent, taking readings every second within a 20 minutes, after which the cable was left to stabilize for 10 minutes, this was done at a controlled temperature of 25 Celsius degrees, we shows a graph of the linear regression below.



Figure 3

# **Results and Discussions**

Once characterized the Nickel-Chrome alloy wire spool, the sensor fabricated, we tested for leak location. The leak was intentionally provoked by immersing a sensor section of 10 cm right in the middle of 1 meter sensor length in a bottle with 200ml of gasoline. The sensor response occurred at 40 minutes of exposure; the figure 4 shows the front panel and the location of the leak.

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Figure 4

The section "Parámetros de Configuración (Configuration Parameters)" lets us enter values as well as resistance AtRho, "B" which is presented by the contacts of the sensor cable and also all sensor length.

# Conclusions

The obtained results shows the leak location in a timely manner, the behavior of the sensor in the presence of a hydrocarbon was expected, in addition the fabrication cost is no more than 40 USD for a length of 100 meters, advantages of this sensor are the AC management, reducing the likelihood of spark, response time also considering the large leakage is greatly reduced by the flow present of these kind of leakage.

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# POLYMER INFILTRATION IN RUGATE POROUS SILICON TEMPLATE IN THE PREPARATION OF HIGHLY FLEXIBLE PHOTONIC POLYMER REPLICAS

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#### Abstract

Photonic crystals containing rugate structure result in a mirror with high reflectivity in a specific narrow spectral region and are prepared by applying a computer-generated pseudo-sinusoidal current waveform. Well defined 1-dimentional photonic polymer replicas showing a reflectivity have been successfully obtained by the removal of rugate porous silicon (PSi) template from the polystyrene composite film. These replicas are stable in aqueous solutions for several days without any degradation. The methods have been provided for the construction of photonic structures with polymers.

#### Introduction

In recent years, the fabrication of nanostructures and microstructures based on porous templates has been intensively investigated [1–5]. The deposition of specific materials into porous templates allows tailoring structures as inverse replicas of the pores. One interesting application for these structures is the infiltration of the air holes with an organic material such as polymers. In addition, polymer devices are inexpensive and disposable. Replications the process of filling the external and/or internal pores of a solid with a different material, and physically or chemically separating the resulting material from the "mold" or "master". Replica polymers, metals, and semiconductors have been prepared from solids with pores on the length scale of nanometers to microns. These template materials have included nanoporous membranes, anodic alumina, and clays.

Porous silicon is an attractive candidate for use as a template because it can be fabricated with high precision and uniformity in a large scale and because the porosity and average pore size and pore depth can be tuned by adjusting the electrochemical preparation techniques [6-10] PSi offer many advantages as a chemical sensing platform. The porous layer contains a high specific surface area for analyte adsorption (in the range of a few hundred m2 per cm3). However porous silicons are limited by their chemical and mechanical stability for many applications, because these films are very brittle. PSi photonic crystals can be fabricated from highly doped p-type silicon by applying a sinusoidal anodic current during an electrochemical etch. This etching waveform produces a porous film with a periodic modulation in porosity and refractive index in the <100> direction of the silicon wafer, resulting in an optical structure known as a rugate reflector. The reflectivity spectrum contains a sharp spectral peak at a wavelength corresponding to the period of the sinusoidal etching waveform.

The mechanism of polymer infiltration into the PSi templates is also very important, the degree of infiltration of polymer solution into the pores of a PSi film depending on annealing temperature, molecular weight, the pore size, solution concentration of polymer, solvent quality, polymer structure, drying conditions, and the surface-interaction energy of the two materials (e.g. hydrophilicity in oxidized PSi and hydrophobicity in freshly PSi). Good solvents tend to cause a swelling of the polymer coils and bad solvents a chain contraction, and  $\Theta$  solvents induce an ideal chain conformation as an intermediate state [11-14].

# Experimental

Preparation of Rugate PSi Samples.

Rugate PSi samples were prepared by an electrochemical etch of heavily doped p++-type silicon wafers (boron doped, <100> oriented, with an average resistivity of 1.0 m $\Omega$ -cm2, (Siltronix, Inc.). Optical reflectivity spectra were measured using a tungsten-halogen lamp and an Ocean Optics S2000 CCD spectrometer fitted with a fiber optic input. The etching solution consisted of a 3:1 volume mixture of aqueous 48% hydrofluoric acid (ACS reagent, Aldrich Chemicals) and absolute ethanol (ACS reagent, Aldrich Chemicals). Rugate PSi samples were prepared by using a computer-generated sinusoidal current waveform. Five different current density waveforms were used in this study. The etch waveform consisted of 160 cycles varied between 20 and 212.5 mA/cm2,. Periodicity was manipulated to obtain wavelengths of peak reflectivity within the visible spectral range, typically on the order of 5-7 seconds.

Free-standing rugate PSi films were obtained from the silicon substrate by an applying of electropolishing current at 60 mA/cm2 for 100 seg in an solution consisted of a 1:10 volume mixture of aqueous 48% hydrofluoric acid. The free-standing freshly-etched samples were rinsed with ethanol and dried in a stream of nitrogen gas.

Infrared Spectroscopy: Surface modification was verified through attenuated total reflectance Fourier-transform infrared (ATR-FTIR) spectroscopy. Spectra were recorded using a Thermo Scientific Nicolet 6700 FTIR with a Smart iTR diamond ATR attachment.

Scanning Electron Microscopy: Scanning electron microscopy (SEM) images were obtained using FEI Quanta 600 instrument operating at an accelerating voltage of 20 kV. Photonic polymer replicas were sputter-coated with chromium prior to acquisition to avoid sample charging.

Preparation of Photonic Polymer Replicas using oxidized Porous Silicon.

Free-standing rugate PSi films were thermally oxidized in the furnace at 800 °C for 3 h. In a typical preparation, a solution of polystyrene (General Purpose Polystyrene, GPPS), av. Mn 113200 g/mol) in toluene/cyclohexene (8:2 ratio) 18.5% by weight, was cast on the top surface of oxidized rugate porous SiO2 film. Then oxidized rugate PSi matrix were removed in HF solution consisting of 48% aqueous HF, ethanol and H20 in a 1:1:3 ratio for 4 h.

Preparation of Melt-Processible Photonic Polymer Replicas using oxidized Porous Silicon.

Free-standing rugate PSi films were thermally oxidized in the furnace at 800 °C for 3 h. In a typical preparation, PE film (Aldrich, Polyethylene High Density, av. M.W. 125,000 g/mol) was melting cast into the porous SiO2 film and the sample was in a hot plate at 180 OC for 1.0 min. Then oxidized rugate PSi matrix from the composite films were removed in HF solution consisting of 48% aqueous HF, ethanol and H2O in a 1:1:3 ratio for 3 h.

# **Results and Discussion**

In this report, we describe a method for fabricating flexible photonic polymer replicas by castsolution varying of solvent quality to study polymer infiltration. In a previous work, Sailor et al,[9] prepared photonic replicas from variety of polymer using oxidized PSi matrix.

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In this work, we develop the replication process using freshly PSi matrix since many polymers are degraded in acidic solutions particularly in HF. This limited for some biomedical application such as biosensing. To overcome this issues, we have prepared freshly PSi matrix with rugate photonic structure. The resulting rugate PSi film was lifted off from the silicon substrate to obtain a free-standing PSi films by applying of lift-off current in a solution of HF and ethanol. The reflection band of freshly PSi films appears at 695.56 nm. Then, polystyrene has been dissolved in toluene and cast on the top surface of rugate PSi film. The resulted composite film was annealed in an oven at 80 °C to fill the pores with the polymer. The reflection band of oxidized rugate PSi/polystyrene composite film appears at 819.85 nm shifted to longer wavelengths upon introduction of the polymer into the pores, due to an increase in the average refractive index of the multilayers, indicating the replacement of a significant amount of empty pore volume with the polymer. After removal of freshly porous silicon film in a basic solution, the photonic polymer replica was obtained at 590.96 nm. Figure 1 shows the intensity of reflected light from the composite in basic solution as a function of time for remove PSi template from photonic polymer replica.



Figure 1. Intensity of reflected light from the composite FPSI/polystryrene replica containing rugates structures from freshly PSi matrix



Figure 2. Optical photograph of flexible photonic polystyrene replica containing rugates structures from freshly PSi matrix.

Photograph of rugate-structured polymer replica is shown in Figure 2 and illustrates that its green color results from the reflection of the polymer replica. The polystyrene replica exhibits a sharp reflection peak in the reflectivity spectrum and replicates the photonic feature of rugate PSi master. The polymer replica is also highly flexible and displays significantly improved mechanical stability without apparent degradation.

Is important to note that replication using freshly PSi films is an important alternative method, instead photonic polymer replicas from oxidized PSi films, since many polymers are degraded in acidic solutions particularly in HF. For some biomedical application such as biosensing, a stable interface between the pores and an aqueous environment is necessary.

Photonic polymer replicas from oxidized porous silicon matrix.

We have prepared PSi matrix with rugate photonic structure. The resulting rugate PSi films was lifted off from the silicon substrate to obtain a free-standing PSi films by applying of lift-off current in a solution of HF and ethanol. Thermal oxidation of these films was carried out in the furnace at 800 °C for 3 h. The reflection spectrum for the oxidized rugate PSi films exhibits its reflectivity shifted to shorter wavelengths due to the decrease of an average refractive index from silicon to silicon dioxide. The general scheme followed in the fabrication of porous Si photonic crystals templates, PSi/polymer composites and polymers imprints is shown in Figure 3.



Figure 3: General scheme followed in the fabrication of porous Si photonic crystal templates, porous silicon/polymer composites, and polymer imprints.

After the thermal oxidation of rugate PSi film, polystyrene has been dissolved in toluene and cast on the top surface of oxidized of rugate PSi film. The resulted composite film was annealed in an oven at 80 °C to fill the pores with the polymer. The reflection band of oxidized rugate PSi/polystyrene composite film appears shifted to longer wavelengths upon introduction of the polymer into the pores, due to an increase in the average refractive index of the multilayers, indicating the replacement of a significant amount of empty pore volume with the polymer. Since one side of oxidized rugate PSi films are coated with the polymers, the oxidized rugate PSi matrix from the composite films can be easily removed in dilute aqueous HF solution. After removal of oxidized rugate PSi from the composite film, the polymer replica was successfully obtained and exhibits its reflection band to shorter wavelengths. This shift indicate that the removal of oxidized rugate PSi template by chemical dissolution results the decreased of the refractive index.

# Conclusions

The rugate-structured photonic polymer replica showing a very high reflectivity using freshly and oxidized porous silicon multilayer. The photonic polymer replicas are robust and flexible. They exhibit an excellent reflectivity in reflection spectrum. We also demonstrate the applications of the flexible devices for sensing vapor sensor. The methods have been provided for the construction of highly flexible photonic structures with polymers.

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## OSCILLATORY DYNAMICS OF FLEXOELECTRIC MEMBRANES IN A VISCOELASTIC MEDIA

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This paper presents a simple model consisting in a second order linear differential equation that describe a thermodynamic phase system (Viscoelastic liquid/Solid-elastic membrane/Viscoelastic liquid) in terms of the evolution of the curvature membrane in terms of a macroscopic force (electrical field) and rheological and surface properties in the system. The model requires eight materials parameters, four for the liquid viscoelastic fluids, three for the elastic-membrane (bending and torsion) and the last one is the amplitude of the macroscopic field (electrical field). In non-dimensional form, the model can be described through three dimensional groups associated to inertial, bulk-viscous and elastic mechanism. The model is analyzed for externally imposed oscillating electric fields and the storage, loss moduli, power and average power are calculated as a function of the viscoelastic properties. The key findings are: (i) the non-dimensional model contain several particular cases depending on the value of the materials properties, (ii) due to the nature of the linearity, the model leads to study particular cases though dimensional numbers, (iii) All equations is this work are analytical and can be extended to others linear models [1-3].

Keywords: flexoelectric membranes, viscoelastic liquid, Storage and Loss moduli, Electrical field.

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# SYNTHESIS AND CHARACTERIZATION OF FLEXIBLE AROMATIC POLYAMIDES, FOR USE AS PROTON EXCHANGE MEMBRANE FOR FUEL CELLS

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# ABSTRACT

Several aromatic copolyamides based on the aromatic diamine 4,4'-(Hexafluoroisopropylidene)-bis-(pphenyleneoxy)-dianiline , which was combined with different molar concentrations, up to 55 mol %, of 2,4-Diaminobenzenesulfonic acid were reacted with equimolar amounts of isophthalic acid to produce copolyamides with increasing sulfonation degree, between 20,and 55%. The synthesis was carried out using Yamazaky's method [1], with controlled amounts of CaCl<sub>2</sub> [2], which generated a copolymer with a maximum inherent viscosity of 0.6549 dL/g. Membranes from all copolymers were cast by dissolving each polymer in dimethyl acetamide (DMAc). The solutions were filtered in a porous glass. The solvent in the solution was evaporated slowly. Then, the remaining solvent was removed at 180°C under vacuum. The resultant membranes were characterized by FTIR, TGA, and DMA. For their use on PEM cells, it was also determined the percentage of water absorption (% WA). These membranes are flexible and the results show that they can be a good prospect for use in PEM fuel cells.

# INTRODUCTION

Actually in the world, there exist a need of finding an appropriate substitution for our major energy system, more efficient and that it would generate less pollution. During the 60's NASA required other forms of energy systems to support independent energy devices for aerospace crafts. They used a system known as fuell cells that contain polymeric electrolyte membranes based on fluorinate polymers such as Nafion<sup>TM</sup> [3-4]. While they were effective for this purpose, they had a lifetime of only 500 h. which limited their use during missions. Since then, other membranes have been proposed with different structures of fluorinated chains, just fluorine containing, sulfonated aromatics, post sulfonated engineering polymers, aromatic polyamides, etc. It has been shown that sulfonated aromatic polymers, such as aromatic polyamides, have shown protonic conduction as good as that of Nafion<sup>TM</sup> in some instances [5].

# EXPERIMENTAL SECTION

The monomers utilized for preparation, 4-4' (Hexafluoroisopropylidene) bis p phenyleneoxy) dianiline (HFD,386669), 2-4-Diaminobenzenesulfonic acid (DABS,32778) and isophthalic acid (ISO,I19209). The solvents employed were: 1-Methyl -2-pyrrolidinone, anhydrous 99,5% (NMP,328634), triphenyl phosphite 97% (TPP,T84654), pyridine 99% (Py,243086). Were used as received from Aldrich Chemical co, without further purification. The technique employed for polymer synthesis as well as for the sulfonated copolymer was Yamazaky's reaction as indicates in Scheme 1 with DABS concentrations from 20 to 55 mole %.



Scheme 1. Schematic Reaction to Obtain the HFD-co-DABS/ISO

The polyamide and sulfonated copolyamides were dissolved in dimethyl acetamide, DMAc, the thickness of all films was in the range 0.03 to 0.09 mm. It was possible to prepare a film with thickness 0.23 and 0.24 mm. The infrared measurements were performed in a FTIR Nicolet Protégé 460 in the transmittance mode by deposition of a solution of the polymer on KBr. The inherent viscosities  $(\eta_{inh})$ of all polymers were determined using a Cannon-Ubbelohde viscometer N° 50 at 30°C at a polymer concentration of 0.5 g/dL in DMAc. The reported value is an average of ten measurements. Furthermore, the thermal decomposition of all copolymers was measured by thermogravimetrical analysis in a TGA-7 Perkin-Elmer Inc. under nitrogen atmosphere between 50 to 800°C at a heating rate of 10°C min<sup>-1</sup>. Previously, each film was dried at 180°C under vacuum for 48 h. The water uptake of all copolymers was estimated by gravimetric analysis. The water absorption for each membrane was determined at 30, 45, 60 and 75°C in a capped test tube immersed in a water bath. At the end of this time the membranes were dried with a soft tissue paper and weighted immediately  $(W_d)$ . Finally, they were dried under vacuum at 130°C for 24 h and weighted again (W<sub>s</sub>). The proton conductivity was obtained by electrochemical impedance spectroscopy using a Potentiostat-Galvanostat AUTOLAB PGSTAT 302 Eco Chemie, with the EIS module over a frequency range of 1 to  $10^6$  Hz. The membranes were activated with  $H_2SO_4$  as suggested by X. Shang et al [6]. It was also determined by DMA-7 Perkin-Elmer as a function of temperature, the different transitions for tan  $\delta$  [7], between 50 and 280°C with a scanning rate of 5°C/min and a probe length of 5 mm.

### **RESULTS AND DISCUSSION**

For the reactions, the addition  $CaCl_2$  ranged between 10 and 27.5%, to increase the polymer reaction yield and eliminate the possibility of back reaction. The fiber size increased with increasing concentration of sulfonic acid groups. The behavior of inherent viscosity, a measure of copolymer molecular weight (MW), was found in the range of 0.38 to 0.65 dL/g. As can see in Table 1, the inherent viscosities do not show a dependence on the concentration of the sulfonate groups in the copolymer.

Table 1. Inherent viscosities		
Polymer	$\eta_{inh}\left(dL/g\right)$	
HFD/ISO	0.61	
HFD-co-DABS/ISO 80-20	0.47	

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HFD-co-DABS/ISO 70-30	0.65
HFD-co-DABS/ISO 60-40	0.53
HFD-co-DABS/ISO 50-50	0.38
HFD-co-DABS/ISO 45-55	0.47
	4.0

The rigidity of the membrane films increase with increasing sulfonation degree.

**%WA** Percentage water uptake of the membranes was determinate by immersion of membranes in deionized water at 30, 45, 60 and 75°C for 24 hours. It was observed that the membranes did not break in these conditions and they did not dissolve. The results are show in the figure 1. As can be seen, as the content of sulfonic groups increases in the copolymer, there is a larger water uptake. The highest percentage of water uptake is the 44% for the copolymer with a molar content of 55% (HFD-co-DABS/ISO 55-45).



Figure 1. Water Absortion of HFD and HFD-co-DABS sulfonated copolyamides.

**FTIR** The IR spectra shown in the Figure 2 of the synthesized HFD polyamide and HFD-co-DABS/ISO copolyamides were used to analyze characteristic band of the  $-SO_3H$  groups in the copolymer chains. The amide groups are found between 3270 and 3310 cm<sup>-1</sup>. On the other hand, the groups at: C=O at 1660 cm<sup>-1</sup>, S=O at 1408 cm<sup>-1</sup>, O=S=O at 1059 cm<sup>-1</sup>, C-S at 1016 cm<sup>-1</sup>, S-OH at 928 cm<sup>-1</sup> and C-S at 680 cm<sup>-1</sup>.



Figure 2. FTIR of HFD and HFD-co-DABS sulfonated copolyamides.

TGA measurements were utilized to evaluate the thermal properties of the membranes. Figure 3 shows the degradation of sulfonics groups from 281°C to 439°C for membranes HFD/ISO and copolymer Second US-Mexico Meeting "Advanced Polymer Science" and XXIV SPM National Congress Riviera Maya, Q. Roo, México. December 2011

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with sulfonics groups concentrations of 20, 30, 40 and 55 mole%. For HFD-co-DABS/ISO the range of loss for the sulfonics groups is between 281°C to 353°C. All membranes were stable up to 280°C. These results indicate that the water molecules leave the membrane in the range of 50 to 281°C similar to the values reported for other sulfonic membranes [8-10].



Figure 3. Thermal descomposition thermograms of HFD and HFD-co-DABS sulfonated copolyamides.

The copolymer membranes were tested in DMA and yielded tan  $\delta$  values, which are shown in Table 2. For the copolymer with higher sulfonation,  $T_{\alpha}$  is 224°C.

	$T_{\alpha}(\bullet C)$	Tan δ
HFD/ISO	241.73	1.279
HFD-co-DABS-ISO 80-20	237.88	11.615
HFD-co-DABS-ISO 70-30	253.52	9.875
HFD-co-DABS-ISO 60-40	245.52	0.251
HFD-co-DABS-ISO 50/50	224.73	0.121

Table 2.  $T_{\alpha}$  and Tan Delta by DMA

Provide the second seco

Figure 4. Tan δ HFD and HFD-co-DABS sulfonated copolyamides

The proton conductivity was determined by AC impedance. It was observed in the results, that a increase of proton conductivity in membranes that have increased concentration of sulfonics groups. The maximum conductivity of these membranes, occurred with HFD-co-DABS/ISO 45-55 with 0.432 mS cm<sup>-1</sup>.

Serie	% Sulfo nation	l tickness (cm)	R' (ohm)	Proton Conductivity S cm <sup>-1</sup>
HFD/ISO	0	0.006	78.545	8.8E-05
HFD-co-DABS/ISO 80-20	20	0.006	52.6	1.3E-04
HFD-co-DABS/ISO 70-30	30	0.003	51.309	6.8E-05
HFD-co-DABS/ISO 60-40	40	0.007	11.673	0.0007
HFD-co-DABS/ISO 50-50	50	0.007	7.5292	1.1E-03
HFD-co-DABS/ISO 45-55	55	0.011	2.9428	4.3E-03





# CONCLUSIONS

The results show that these copolymers could be a good option to use into electrolytic membranes in fuel cells. Water absorption is higher for the copolymer with the highest concentration of sulfonic groups to 44%. The degradation of sulfonic groups starts at 291 ° C. The proton conductivity was 4.3 mS cm<sup>-1</sup> for the copolymer with the highest percentage of sulfonation.

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# NONLINEAR OPTICAL PROPERTIES OF POLYCAPROLACTONE FILMS

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# Abstract

Polyurethane polymers are important and versatile materials that have numerous applications in foams, surface and textile coatings, adhesives and elastomers. They are used in a wide variety of industries such as furniture, construction, aircraft and automobile manufacture and mining equipment. We are looking now for other applications, which correspond to nonlinear optical properties found in  $\alpha$ - $\omega$ -telechelic polycaprolactone diols (HOPCLOH) and triblock copolymers that were studied. Synthesis of  $\alpha$ - $\omega$ -telechelic PCL diols was achieved by enzymatic ring opening polymerization with Yarrowia lipolytica lipase immobilized on a macroporous resin Lewatit VP OC 1026, and using diethylene glycol and poly(ethylene glycol) as initiators [1]. Films prepared at different conditions were analyzed only and two films presented nonlinear optical properties. Z-scan technique with an Argon laser was used to determine these optical properties. Nonlinear optical properties of several materials by this technique were reported [2,3]. We found the presence of nonlinear refractive index due to thermal effects This polycaprolactone is a candidate for optoelectonic applications.

Keywords: Z-scan, Nonlinear optical properties, Polycaprolactone

# Introduction

Polycaprolactones have many applications as injectable materials, part of their advantages are in the green chemistry because they are biodegradable polymers. We choose to study polycaprolactone films because they can be good candidates for infillings where the nonlinear optical applications can help to solve some problems of the human body.

Nonlinear optical properties area have grown in the last years because their application as component in de optical and electrooptical devices have been increasing [4,5]. For a material to become a promising NLO material, its figures of merit must offer a large and fast nonlinear response. The self-interaction of a laser beam in a medium changes the optical properties of the medium, induced by the incident radiation. Consequently, the determination of the nonlinearity is of great importance

Several techniques have been developed to measure the nonlinear properties. Among these methods, the Z-scan technique [6] has been extensively employed due to it characteristic advantages: simplicity, high sensitivity, and simultaneous determinations of sign and magnitude of the nonlinearity.

In this work we study the third order nonlinear optical properties of  $\alpha - \omega$ -telechelic PCL diols films which were prepared as reported [1].

## Experimental

Z-scan technique allows determining both sign and magnitude of nonlinear refractive index  $n_2$ , it is very sensitive to detect small nonlinear refraction. As an excitation source we use a CW Argon laser at 514 nm, at a power of 8-9 mW, this has a Gaussian profile and it is focused by a converging lens (f=180 mm), the beam waist was a 5.9 µm. The films was placed between two acrylic plates with a 50mm x 50mm hole in the center and near the waist of the focused Gaussian Beam and moved in direction of the propagation (z-axis) of the light (See figure 1).



Figure 1. Schematic illustration or experimental arrange

The focal length influence of the photo-induced lens in a nonlinear material with z-scan technique, it is analyzed considering the focal length as dependent on the incident beam radius  $\omega(z)$  at some integer power m. Gaussian beam propagation and thin lens approximation were used to obtain an expression of far field normalized transmittance. Considering the conditions to applied z-scan technique, it is possible to obtain the normalized transmittance of the z-scan experiment as:

$$T = \frac{F^2}{z_0^2 + (F-z)^2} \tag{1}$$

For a thin thermal media it has been demonstrated that the focal length photo-induced by the Gaussian beam is given by:

$$T = \frac{\pi k}{P_{abs} \left(\frac{\partial n}{\partial T_i}\right)} w^2 \tag{2}$$

Where  $\kappa$  is the thermal conductivity, P is the absorbed power, and  $\frac{\partial n}{\partial T_i}$  is the charge of refractive

index with the temperature.

Reynoso-Lara et al. [7] considering that a nonlinear medium, with refractive nonlinearity, illuminated by a Gaussian beam can be modeled as a lens with a focal length that depends on the beam radius to some integer power,  $F = a_m \omega^m(z)$ , where  $a_m$  is a constant with the adequate units that can have parameters of the material, and m is an integer number. Using a weak lens approximation, and substituting F and w(z) the transmittance by z-scan model is:

$$T = 1 + \frac{2z}{F_{om} \left[1 + (z/z_0)^2\right]^{\frac{m}{2}}}$$
(3)

Where F0m=amw0m is the shortest focal length of the photo-induced lens. From this expression it is possible to calculate the position of the peak and valley of the z-scan curve, giving the following relation

$$z_{p-v} = \left| z_{peak} - z_{valley} \right| = \frac{2}{\sqrt{m-1}} z_0$$
(4)

Knowing these positions it is possible to calculate the difference between the transmittance at the peak and valley to obtain:

$$\Delta T_{p-v} = \left| T_{peak} - T_{valley} \right| = \frac{2k}{a_m w_0^{m-2}} \left[ \frac{(m-1)^{m-1}}{m^m} \right]^{1/2}$$
(5)

Where k= $2\pi/\lambda$ .

The following formula models the transmittance in parameters a,  $\omega$  and m.

$$T = \frac{1}{1 - \frac{4x}{(1 + x^2)^2} \left(\frac{z_0}{2F_{0m}}\right) + \frac{4}{(1 + x^2)^2} \left(\frac{z_0}{2F_{0m}}\right)^2}$$
(6)

where  $x = z / z_0$  and the relation between  $\Delta \Phi_{om}$  and the parameters is:

$$\Delta\Phi_{0m} = \frac{z_0}{2F_{om}} \tag{7}$$

### **Results and Discussion**

We analyzed all samples but only two can be possibilities for measuring the nonlinear optical properties, this are named, 4EG and 7TEG. Figure 2 show the transmittance of the z-scan experiment to samples, after applied the model described before we obtained an adjusted curve, and can be obtain the focal length photo-induced ( $F_0 = a_m \omega_0^m$ ). We conclude that the nonlinearities are originate by thermal effects due that experimental data gives better adjustment using m=2 [8]. Table 2, show the focal length photo-induced and correlations obtained by adjust for the model. Due to origin of the nonlinearities, are induced a negative lens, with focal length of 11.2 and 14.7 mm, respectively.



Table 1. Focal length photo-induced to sample 4EG and 7TEG.

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Sample	Power	focal length	Correlation	
	(mW)	photo-induced (mm)		
4EG	9	11.2	.97	
7TEG	8	14.7	.98	

### Conclusions

Polycaprolactones present nonlinear optical properties and can be used to design an optical limiters.

### Acknowledgements

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# COUNTERION EFFECT ON THE MORPHOLOGY AND ELECTRICAL PROPERTIES OF POLY(3,4-ETHYLENEDIOXITHIOPHENE) DEPOSITIONS

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### Abstract

In this work, electropolymerizations of PEDOT in aqueous solution were carried out. Nanometric graphite layers (NGL) deposited on glass were used as the electrodes. Counterions such as dodecyl sulfuric acid (DSA) [2], 4-dodecylbencenesulfonic acid (DBSA) [3] or polystyrene sulfonic acid (PSS) [3] were evaluated to study their effect on PEDOT morphology and electrical conductivity. PEDOTs' morphology was characterized by atomic force microscopy (AFM) and scanning electron microscopy (SEM), and electrical properties by electrochemical impedance spectroscopy (EIS). Microscopy techniques showed that the longer the counterion alkyl chain, the greater the particle size and the greater film thickness. According to this, PEDOT:DBSA films presented the largest particle size and thickest films and also the best conduction in comparison with PEDOT:PSS or PEDOT:DSA.

### Introduction

Morphology is a very important characteristic of polymers and largely determines their properties. Of course, morphology in intimately related to the synthesis conditions [4]. The choice of a synthetic method depends on the type of CP and the macroscopic form of it. A chemical bulk method produces the polymer as powder and the electrochemical polymerization produces the material as a thin film [5].

The electrochemical polymerization involves the oxidation of monomers such as 3,4ethylenediopxithiophene (EDOT) (Figure 1). In this process, the polymerization initiates at the electrode/electrolyte interface that promotes the formation of a polymeric film that adheres to the electrode surface [6]. Polymerizations at constant current are more convenient for controlling the thickness of the deposited films [7].



Figure 1. 3,4-Ethylenedioxithiophene (EDOT) monomer.

EDOT monomer has very poor solubility in water (2.1 g/L). Furthermore, electrochemical polymerization of EDOT is inhibited by water molecules interacting with thienyl cation radical, the polymerization intermediate. To solve these problems, it was recently proposed to add significant amounts of anionic surfactants to aqueous solutions of EDOT. The use of a surfactant for electropolymerization of heteroaromatic compounds has several important effects. The presence of micelles provides an interesting solvent system for solubilization of these water insoluble compounds. Moreover, the addition of surfactants to the electrolyte can stabilize charged species such as anions or cation radicals, and can also improve the properties of conducting polymers [8].

The aim of this work was to evaluate the effect of the three evaluated counterions on morphology and electrical properties of PEDOT salts electropolymerized, in aqueous medium, by a potentiostatic mode electropolymerization.

# Experimental

# **PEDOT** salts electropolymerization

In oxidative polymerization the monomer is oxidized at the electrode surface, releasing an electron to become a radical cation. Two radical cations react to form a dimer, which immediately splits off two protons. The neutral dimer is then readily oxidized to generate a radical cation, which continues the process of chain growth, eventually producing a polymer [9].

Films of PEDOT salts were electrochemically deposited on top of NGL working electrode, a Sigma Aldrich Ag/AgCl electrode as reference electrode, and a Pt wire counter electrode, using a three-electrode electrochemical cell in a Solartron Instrument.

The monomer (EDOT) (0.001 moles), the counterion (PSS, SDS or DBSA) (0.001 moles) and distilled water (200 mL) were mixed in a three-necked round bottom flask. This mixture was sonicated in a Branson sonicator at 25 °C, for 30 min, time enough to form a stable emulsion. Once the emulsion was obtained the three electrodes were immersed to perform polymerization. Solatron Analyzer equipment was used as the power source.

The reactor was perfectly closed to prevent monomer evaporation. The emulsion was deoxygenated by bubbling  $N_2$  for 20 min prior to all electropolymerizations. The experiments were performed at room temperature under N2 atmosphere. The electropolymerization and deposition of PEDOT were carried out using the potentiostatic mode, applying a 1.5 V for 2,400 s. At the end, the NGL electrode with the deposited polymer was removed of the reactor and washed with distilled water (10 mL).

# Characterization

The topography, morphology and thickness of the deposits were analyzed by: SEM using a JEOL JSM-7401F Field Emission microscopy, with ultra high vacuum and 1 nm resolution. AFM characterization was carried out in tapping mode, with a VEECO SPM MultiMode AFM system, using a 225  $\mu$ m probe.

EIS analyses were carried out with a Solartron Analyzer, model 1260 and 1287. The interface software used was Z-Plot, in which the AC voltage (100 mV and 50 mV) and the frequency (1E6 Hz to 0.1 Hz) were set. The configuration was a three-electrode electrochemical cell, used to carry out the electrochemical polymerization and as electrolyte the aqueous micellar solution.

# **Results and Discussion**

PEDOT synthesized is in its conductive form, the oxidized form. In this state PEDOT contains positive charge carriers, which were offset by incorporating anions (PSS, DSA or DBSA) from the electrolyte (aqueous micellar solution), or counterions, with the aim of maintain the electroneutrality and improve the polymer stability in an aqueous medium.

The type of counterion affects PEDOT properties in different ways. First of all, both the size and

shape of ions, which have a considerable effect on the diffusion rates inside the polymer matrix, limiting the oxidation and reduction rates of the polymer, and second, determine the morphology and conductivity of the polymer.

Figure 1-a shows the surface of PEDOT:PSS cauliflower-like film electrochemically deposited formed by small shperoydal particles, whit few nanometer diameter (figure 2-b), this is a rough surface, and we confirm this by looking at the 3-D image (figure 2-c). SEM image (figure 2-d) allow us to estimate the film thickness,  $\approx 500$  nm, and also we can observe the NGL deposition used as electrode, this film was deposited on to the glass slide, with  $\approx 200$  nm thickness, and is conductive enough to carried out the CP deposition.



Figure 2. a) AFM tapping mode image of PEDOT:PSS deposition, b) the height and particle size evaluation, c) 3-D visualization of the film topography, d) SEM image of film thickness and e) PSS counterion.

The topography of the deposited PEDOT:DSA film is illustrated in Figure 3. As it is observed, the surface is clearly rough as shown in the 3-D graphic, and the microstructure or the polymer particles shape is also spherical, but these have larger diameters than PEDOT:PSS (~1.5  $\mu$ m). The PEDOT:DBSA salts deposited is the thicker one, with ~4  $\mu$ m height (Figure 4(d)), this is due the DBSA is the larger counterion used. And as the Figure 4(b) shows the particle diameter is 2  $\mu$ m, and also the microstructure is shperoidal.



Figure 3. a) AFM tapping mode image of PEDOT:DSA deposition, b) height and particle size evaluation, c) 3-D visualization of the film topography, d) SEM image of film thickness, and e) DSA counterion.



Figure 4. a) AFM tapping mode image of PEDOT:DBSA deposition, also b) the height and particle size evaluation, the c) 3-D visualization of the film topography, d) SEM image of film thickness, and e) DBSA.

As mentioned, morphology has an important effect on conductivity; the values of conductivity in S/cm are shown in Table 1. These values were obtained by EIS of the deposited films, the high value is 2.4E-8 S/cm, and is for PEDOT:DBSA film. The lowest conductivity value was for the PEDOT:PSS deposit, with 1.02E-9 S/cm.

PEDOT:	PSS	DSA	DBSA
Resistance ( <b>Ω</b> )	1,290.10	1186.8	437.2
Capacitance (F)	5.77E-10	5.09E-10	9.73E-10
Film thickness (cm)	4.0E+06	1.0E+06	5.0E+05
Conductivity (S/cm)	1.02E-09	4.42E-09	2.40E-08

Table 1. Resistance and Capacitance of PEDOT salts deposited, measured by EIS.

# Conclusions

SEM and AFM showed that anions chain length has a determining effect on the polymer morphology, the larger the counterion, the thicker the film deposited. EIS measurements let us to determine resistance and capacitance, allowing calculating conductivity. These values showed that conductivity was also importantly affected by counterion length, indicating that the larger the counterion, the higher the conductivity.

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# CHARGE TRANSFER IN POLYTHIOPHENE-TITANIUM COMPOSITES SYNTHESIZED BY PLASMA

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The use of polythiophene (PTh) as a photoactive material in solar cells has been considered since 1982, however the poor efficiency of the prototypes developed has led to a rapid decline of this research field. Recently, the discovery of an ultrafast and efficient photoinduced electron transfer between conjugated polymers and fullerenes has represented an important step in the revival of organic photovoltaic devices. It has been found that some polymer-metal semiconductor composites form stable matrices that retain the electronic distribution of conjugated polymers. When inorganic materials of high electron affinity are added, the composites can be used in photovoltaic devices [1-3]. One of those composites are polythiophenes with photoactive materials like titanium oxides [4-6].

In this context, in this study the morphology, structure and charge transfer in thin films of polythiophene, iodine doped polythiophene and composites of both kind of polymers with titanium are presented. The studies were conducted from the perspective of potential application in solar cells. The characterization was made using electron microscopy, atomic force microscopy, and IR and UV-vis spectroscopies.

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# OPTICAL PROPERTIES OF METHACRYLIC COPOLYMERS CONTAINING PHENYLENE-SUBSTITUTED AZOBENZENE COMPOUNDS

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In recent years, photoreactive organic materials have attracted much attention because of their potential applications in different technologies like optical displays, holographic storage and photomechanics [1-2]. Among the photoreactive organic materials the azobenzene polymers have shown to be particularly effective for holographic storage because of their good photoresponsive properties when they are irradiated with a polarized laser light. In this work we present the synthesis and optical characterization of a new series of copolymers bearing phenylene-substituted azobenzenes (73, 47, 32, 28, 16 and 5 % mol). The response to photoisomerization was evaluated by UV-Vis spectroscopy in solution and in thin films, irradiating with a laboratory UVP lamp (365 nm wavelength). Birefringence was induced by a semiconductor laser beam of 413 nm of wavelength and intensity of 20mW cm<sup>-2</sup>. Best results were observed in copolymers 32, 28 and 16 % mol, which also developed regular holographic gratings over thin films when they were irradiated with circularly polarized light. Holographic gratings were analyzed by Atomic Force Microscopy (AFM) and Polarizing Optical Microscopy (POM).

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# PREPARATION AND CHARACTERIZATION OF HYDROPHILIC MEMBRANES BASED ON POLYETHYLENE GLYCOL (PEG) AND SODIUM ACRYLATE (SA) FOR PERVAPORATION OF WATER/ETHANOL MIXTURES.

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### Abstract.

The present work is on the preparation and use of four hydrophilic polymeric membranes for ethanol dehydration by pervaporation. The membranes were synthesized based on hydrophilic random copolymers from polyethylene glycol (PEG) and sodium acrylate (SA); prepared by random copolymerization with aromatic polyamides (PA) and styrene (St), respectively. The synthesis of the material based on PEG was made through direct polycondensation with different functional groups and the copolymer materials based on SA were synthesized in emulsion by free radicals polymerization, with different concentration of the hydrophilic component. Copolymers were characterized by FTIR, TGA and DSC for determining functional groups and thermal stability, respectively. Swelling test, show water and ethanol retention capacity of these membranes. Pervaporation measurements were performed to determine if membranes had the capacity for ethanol dehydration.

### Introduction.

Pervaporation (PV) is a membrane technology, considered one of the most effective and energysaving separation processes. Also it demonstrates significant advantages over existing separation processes, such as high selectivity for azeotropic mixtures separation, low-cost modular construction, they had the capacity to participate in hybrid systems and due to mild operations, no emission to pollutants towards the environment [1-4].

However, the PV process has limited flux because permeation can occur mainly by diffusion across the membrane thickness. Nonetheless, there exist many ways to improve the fabrication of membranes with better PV, such as increasing the hydrophilicity of the membrane by incorporating hydrophilic moieties into the matrix or designing an appropriate polymer structure. For that reason, preparation of new materials for membranes with good PV performance is key for developed this kind of membranes separation process.

In this work the preparation of membranes based on polyethylene glycol (PEG) and sodium acrylate (SA) as hydrophilic components, results attractive due to their high affinity and capacity for water retention. Synthesis of copolymers based in PEG, copolyether-amides, was made through direct polycondensation [5], using isophthalic acid (ISO), or 5 t-butylisophthalic acid (TERT) and 4,4'-(hexafluoroisopropylidene) diamine (HFA) in each case. On other hand, copolyacrilates or copolymers based on SA, were copolymerized with styrene by synthesis in emulsion by free radicals polymerization [6], the concentration of the hydrophilic component were 25% and 30% w/w. With the purpose of prepare novel materials for PV and determine their capacity to dehydrate ethanol.

### **Experimental.**

### Materials.

Copolyether-amides. The monomers 4,4'-(hexafluoroisopropylidene) diamine (HFA), the aromatic dicarboxylic acids isophthalic acid (ISO), 5-tert-butylisophthalic acid (TERT) and polyethylene glycol (2000  $g \cdot mol^{-1}$ ) were obtained from Aldrich Chemical, Co. (Saint Louis, MO) and used as

received. Reagent-grade calcium chloride was dried under vacuum at 180 °C before use. N-methyl-2-pyrrolidinone (NMP) 99.5%, pyridine (Py) 99%, and triphenyl phosphite (TPP) 97% were used as received. All reactants were purchased from Aldrich Chemical Co.

Copolyacrylates. Reagent grade styrene was passed through a DHR-4 column (SPP) to remove the inhibitor immediately before use. Monomer of sodium acrylate (SA) 99%, reagents sodium dodecylsulfate (SDS) 99%, hydroquinone and potassium persulfate (KPS) reagent grade, were used as received. All of them were obtained from Aldrich Chemical Co.

# Membrane preparation.

Films of copolyether-amides were cast by dissolving 0.9 g of each copolymer in 1 ml of dimethyl formamide (DMF), and 6 ml of dichloro methane (DCM). The solution was filtered and poured on a glass plate with on an aluminum ring, and the solvents were evaporated at room temperature for 2 h., then they were kept at 40°C for 24 h. Once the film was strong enough, it was dried in a vacuum oven up to 60°C for 24 h. Copolyacrylate's films were diluted by dissolving 0.025 g of each copolymer in 25 ml of a mixture 1:1 v/v of chloroform and acetone. The solution was cast on a petri dish and covered with a funnel at room temperature for 24 h. Finally to avoid residual solvents, it was dried in vacuum for 24 h at 60°C.

# Characterizations.

For all copolymers, the infrared spectrum was obtained using a Fourier transform infrared spectrophotometer, NICOLET Protege 460, taking an average of 100 scans per sample, using a thin film of the copolymers for reading the sample.

Onset of thermal descomposition, Td, measurements for copolymers were performed in a Perkin-Elmer thermogravimetrical analyzer (TGA-7). The tests were carried out on 6-12 mg samples, between 50 and 600 °C, at a heating rate of 10 °C/min under nitrogen atmosphere. Glass transition temperatures for the copolymers were determined using differential scanning calorimetry in a DSC-7 (PerkinElmer, Boston, MA), using 4-5 mg samples, between 50 °C and 350 °C for copolyether-amides; and 50°C and 200°C, for copolyacrylates. At a heating rate of 10 °C/min under nitrogen atmosphere.

# Degree of swelling.

Sample's films of 1x1 cm of each copolymer were dried in a vacuum oven for 24 h, after that were immersed in water and/or ethanol for 24 h at different temperatures (35, 40, 45 and 45°C). They were subsequently dry blotted with tissue paper to remove excess solvent and finally weighted. Degree of swelling (DS) of the membranes was defined by the following equation:

Degree of swelling = 
$$\frac{(W_w - W_d)}{W_d} \times 100\%$$

Where  $W_d$  and  $W_w$  denote the weight of dry and swollen membranes, respectively.

# Pervaporation experiment.

A standar pervaporation process equipment [7] was used, with a solvent mixture recirculation using a diaphragm pump. In pervaporation, the feed solution is in direct contact with the membrane. The effective area was  $12.56 \text{ cm}^2$ , and the permeate pressure was kept at about  $7 \sim 8 \text{ mmHg}$  by a vacuum pump. Pervaporation measurements of the membranes was made with a mixture of 80% ethanol and 20% v:v water, at 4 temperatures: 35, 40, 45 and 50°C.

The ethanol contents in the feed, permeate, and retentate were analyzed by UV-spectrophotometry

by the potassium dichromate method [8]. Measurements were made preparing a calibration curve at 585 nm (Spectrophotometer, DU® 650, Beckman Coulter<sup>TM</sup>).

The pervaporation performances of the membrane is generally characterized by its flux and selectivity towards the solvent mixture. Flux is defined by the following equation:

$$J = \frac{Q}{At}$$

where J, Q, A, t are permeation flux  $(g \cdot m^{-2} \cdot h^{-1})$ , total amount of permeation (g), membrane area (m<sup>2</sup>), and operating time (h), respectively. The selectivity is defined as follows:

$$\alpha = \frac{Y_A X_B}{X_A Y_B}$$

where  $X_A$  and  $X_B$  represents the weight fractions of ethanol and water concentrations (wt%) in the feed solution, respectively. And  $Y_A$  and represents the weight fractions of ethanol and water concentrations (wt%) in the permeate.

### **Results and Discussion.**

### Physical properties.

The infrared spectra of copolyether-amides show several bands that are expected for the formation of the polyamides, a carbonyl absorption band at 1660  $cm^{-1}$  and a broad absorption band attributed to the amide group at 3300  $cm^{-1}$ . The polyamides containing the tertbutyl group also show the representative band of the methyl groups at 2960 cm-1. Also, the bands for functional groups of polyether are visible at 2880  $cm^{-1}$  and 1100  $cm^{-1}$ corresponding to vibration of C-H and C-O-C, respectively.

The properties of random copolyether-amides synthesized here are summarized in Table 1. The onset of decomposition temperature,  $T_d$ , for these copolyether-amides is above 430°C, the results indicate that they are very similar. The presence of a single glass transition temperature indicates that there is no phase separation in these materials, a fact that was expected for random copolymers. The case of the copolyether-amide HFAISO-co-PEG, the presence of  $T_g$ , can't be measured due to the fact that the copolymer is rubbery and it was not possible to measure it.

1 abic 1.	able 1. Tropentes of coporyetter-annues with different diacids.							
Mambrona	HFA	ISO ó TERT	PEG	Yield	Thickness	T (°C)	T (9C)	
Mem	Memorane	(mg)	(mg)	(mg)	(%)	(mm)	$I_g(C)$	$I_d(C)$
HFA	ISO-co-PEG	682.183	423.80	1000	85	0.110		430
HFA'	TERT-co-PEG	682.183	566.938	10	90	0.264	281	430

Table 1. Properties of copolyether-amides with different diacids.

--Not available.

For copolyacrylates, the infrared spectra show similar bands, the difference between monomeric structures it's scarcely notable. Both spectrums exhibits a sharp band at 1400  $cm^{-1}$  due to COO-group, associated to SA; and an intense triplet around 3000  $cm^{-1}$ , which is related to styrene. These features of IR spectra confirms the formation of the copolymer; also there appears a C-H flexion at 760  $cm^{-1}$  which is associated with the styrene as well as a peak at 1600  $cm^{-1}$  due to C=C stretching of the aromatic ring.

According to the thermal properties measurements onset of thermal decomposition (Table 2), Td, tends to increasing as the percentage of SA increases. Likewise the  $T_g$ , increases with increased content of SA in the copolyacrylate. This indicates that copolyacrylates aren't a blend of two homopolymers but they are random copolymers.

Membrane	SA (g)	St (g)	Yield (%)	Thickness (mm)	$T_g$ (°C)	<i>T</i> <sub>d</sub> (°C)
SA-co-St (25-75 w/w %)	6.44	18.75	60	0.08	91.47	457
SA-co-St (30-70w/w%)	7.73	19.25	60	0.044	110.29	463

Table 2. Properties of copolyacrylates with different concentrations of component hydrofilic

Swelling test show water retention capacity in copolyether-amides membranes (Figure 1) that presents a maximum swelling at 50°C with a 60 wt % water retention using the HFAISO-co-PEG, meanwhile the polyamide prepared with the bulky nonpolar tert-butyl substituent has an average of 22% of DS in all the temperatures. On other hand, membranes based on SA, had presented zero % of swelling in water.





**Figure 1.** Effect of temperature on the degree of swelling in water through copolyether-amides membranes.

**Figure 2.** Effect of temperature on the degree of swelling in ethanol through copolyacrylates membranes.

In the case of ethanol swelling tests, the copolyether-amides tend to dissolved and lose their structure in contact with ethanol. This behavior indicated that concentration of PEG into the structure of the membrane, were in excess and causes the capacity of dilution of these highly hydrophilic segments into ethanol, for consequence, it was not possible to use these membranes for water-ethanol separation. On other hand, the copolyacrylates show hydrophobic behavior (Figure 2). Results as swelling increases as the ethanol temperature increase, reach a maximum DS of 6.46% at 50°C, in the membrane with 25% w/w of SA.

It was only possible to evaluate the membranes of copolyacrylates, given the fact that the membranes based on PEG, were highly hydrophilic and when in contact with the mixture ethanol water, they lose their structure or were dissolved.

Overall, the total permeation rate increases with an increase in the temperature. When the temperature of the feed solution increases, the permeation rate in general follows an Arrhenius-type behavior. Figure 3 and 4 shows the Arrhenius plots for the permeation rate of the copolyacrylates with 25% and 30% w/w of SA, respectively. The permeate flow dependence as a function of the temperature, makes it feasible to determine the "apparent activation energies ( $E_a$ )", for the pervaporation process trough the membrane.

Membranes with 25% of SA, reach maximum flow at 50°C with 8.4 lt/h\*m<sup>2</sup>\*mm, and present an  $E_a$  of 3.43 kcal/mol, showing greater sensitivity to temperature. On the other hand, the membranes with higher content of SA (30% w/w), showed a maximum flow of 3.75 lt/h\*m<sup>2</sup>\*mm and an  $E_a$  of 6.01 kcal/mol.

The selectivity between membranes of copolyacrylates show a separation factor lower than 0.2.

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These results indicate that despite of the fact that membranes show a hydrophobic behavior, they possess hydrophilic sites that were activated in the systems by the pressure difference. Thus it's reflecting in the pervaporation of both components: water and ethanol. In the final balance both the retentated and permeated show similar concentrations and indication that the pressure differential has set a new equilibrium in the solvent mixture for both sides of the membrane.



**Figure 3.** Arrhenius plot of copolyacrylate with 25% w/w of SA.



**Figure 4.** Arrhenius plot of copolyacrylate with 30% w/w of SA.

### Conclusions

Separation of ethanol/water wasn't achieved using the copolymer membranes proposed in this or because the copolyacrylate's membranes show a hydrophobic behavior under the vacuum conditions tested, the hydrophilic sites were activated, allowing the passage of water and ethanol through the membrane. On the other hand, membranes prepared from copolyether-amides swell strongly in ethanol losing becoming instable for pervaporation measurements. Therefore, the membranes proposed in this work could not be used in the separation ethanol-water since copolyacrylates membranes reached and equilibrium in the pervaporated and retentated at 71% ethanol and 29% of water.

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# REMOSIÓN Cu IN AQUEOUS SYSTEM WITH MODIFIED CHITOSAN

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# Summary

Currently, pollution is a hot topic of global significance, as such investigations have focused on increasing the soil decontamination, but especially in water effluents contaminated with heavy metals (1). In the present investigation was carried out the preparation of anionic chitosan films for use in metal removal, which was used Copper (Cu) in aqueous solutions (2). All measurements made for Cu quantification uses a UV-Visible spectrophotometer. These chemically modified chitosan films was entrusted with a support fabric (3). Also, the films were characterized through the technique of spectrophotometry with Fourier transform infrared (FTIR). Keywords: chitosan, modified, heavy metal contamination.

# Conclusions

Analyses of the chemically modified chitosan films show that the modification if it exists, because in the FTIR spectrum displayed the characteristic signs of sulfation, the region showing these signs is the 900cm-1 corresponding to S-O-C group and the group S=O which is the 1230 cm-1 with it is found that if I meet the desired objective of this research. With respect to the metal absorption test, the results show that if there is a considerable removal of Cu in aqueous solutions of approximately 30% removal of the absorption solution in a static natural chitosan and modified chitosan with respect to a removal of 21%, there is a noticeable difference and this is possibly the pH is modified chitosan.

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# NANOFIBROUS MEMBRANES OF POLY (LACTIC ACID)-G-AM/COLLAGEN BY COAXIAL ELECTROSPINNING METHOD: PREPARATION AND CHARACTERIZATION

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Nanofibrous membranes made out of biocompatible and biodegradable polymers have been studied as scaffolds for tissue engineering. In this work nanofibrous membranes of poly (l-lactic acid) modified with collagen were obtained by the coaxial electrospinning method. The morphology, diameter and porosity were determined by scanning electron microscopy (SEM) and an image analyzing program. The diameter of the fibers varied between 100 and 700 nm. The mechanical properties of the nanofibrous membranes were evaluated by microtensile tests.

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# SULFONATED COPOLYAMIDES FOR POLYMER ELECTROLYTIC MEMBRANES

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### Abstract

Two series of sulfonated random copolyisophthalamides with increasing sulfonation degree were synthesized from the aromatic diamines 4,4'-(hexafluoroisopropylidene)dianiline, *HFA*, or 4,4'-(9-fluorenilidene)diamina, *BFA*, reacted with 2,4-diaminobenzenosulfonic acid, *DABS*, by direct polycondensation. Thin films of the sulfonated copolyamides were prepared by the solution method using dimethylacetamide, *DMAc*. The structure of the resulting sulfonated polyamides was confirmed by <sup>1</sup>H *RMN* and *FT IR*. Their inherent viscosities, Ionic Exchange Capacity, *IEC*, water uptake, *WU*, and proton conductivity,  $\sigma$ , are also reported. The results showed that membranes with > 40% *DABS* presented good Ion Exchange Capacity and water uptake. The value of proton conductivity was close to the one of Nafion tested under the same conditions.

# Introduction

Sulfonated polymers are a kind of ionomers know by their strong ion exchange capacity, particularly cation exchange membranes, for instance, in electrolysis cells and electrodialysis and as resins for treatment of hard water. Sulfonation of a polymer consist in introducing sulfonic groups (-*SO3H*) which render these polymers hydrophilic and proton conductive. The resulting polymers exhibit high ionic conductivity, good mechanical strength and high temperature resistance[1-5]. Aromatic polyamides are considered a class of engineering polymers that are thermally stable; the incorporation of ionic groups into the structure of these polymers could impart them ion exchange properties. Because of the presence of amide groups, aromatic polyamides tend to retain water [6-7]; Depending on their chemical composition, water absorption and proton conduction capacity may be enhanced in these polyamides by increasing concentration of sulfonic acid side groups.

# Experimental

Two series of sulfonated copolyamides with sulfonation degrees, *SD*, between 20 and 50 mol% were synthesized by direct polycondensation following a procedure described first by Yamazaki, with some small modifications[8-9]. The polycondensation reaction was performed with equimolar amounts of the diamine, *BFA* or *HFA*, and diacid, *ISO*, for the *BFAISO* and *HFAISO*, or a controlled combination of non sulfonated and sulfonated diamines, with isophthalic diacid, ISO, for the copolymers, *BFA-co-DABS/ISO* or *HFA-co-DABS/ISO*. The sulfonation degree, *SD*, was controlled by adjusting the ratio of monomer *BFA* or *HFA* to monomer *DABS*. The reaction was carried out using calcium chloride, *CaCl*<sub>2</sub>, N-Methyl-2-Pyrrolidone, *NMP*, as a solvent, with pyridine, *Py*, and triphenyl phosphate, *TPP*, as the transfer reactants.

Thin membranes of the polyamide and sulfonated copolyamides were cast using dimethylacetamide, *DMAc*, as the solvent by the solution-evaporation method.

The structure of the resulting membranes was analyzed and confirmed by *FT IR* using the method of Attenuated Total Reflectance (*ATR*), with an optical microscope coupled to a Fourier Transform Infrared spectrometer Nicolet Protégé 460 taking an average of 50 scans per sample between 600 and 4000 cm<sup>-1</sup>, and *1H RMN*, spectra for copolyamides were obtained in a Bruker 400 MHz *NMR* 

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spectrometer using deuterated dimethyl sulfoxide (*DMSO-d6*) as the solvent and tetramethylsilane (*TMS*) as an internal standard. Inherent viscosities ( $\eta_{inh}$ ) of all polymers were determined in *DMAc* using a Cannon-Ubbelohde viscometer No. 50 at 30°C at a polymer concentration of 0.2 g/dL.

The ability of the membranes to absorb water was estimated by gravimetric analysis. They were immersed in deionized water for 48 h at a fixed temperature (at 25, 45, 65 and 75 °C). The water uptake, *WU*, was calculated according to the following equation:

$$WU(\%) = \frac{Ww - Wd}{Wd} \times 100\tag{1}$$

where Ww(g) and Wd(g) are the wet weight and dry weight of the membranes respectively. Water uptake for polyamides and copolyamides is reported as the average value of at least two measurements.

A potentiometric titration technique was used to determine the Ion Exchange Capacity (*IEC*) of the membranes at room temperature. The *IEC* of the membranes was determined by:

$$IEC(\frac{mmol}{g}) = \frac{V \times M}{wd}$$
(2)

where V (ml) and M (M) are volume consumed and the molar concentration of NaOH, respectively. wd (g) is the membrane dry weight. *IEC* is reported as the average of at least two measurements.

Proton conductivity was measured by electrochemical impedance spectroscopy using a Potentiostat-Galvanostat AUTOLAB Model PGSTAT12/30/302 with the EIS module over a frequency range of 106 to 1 Hz with oscillating voltages of 50 *mV*. *Nafion*® 115 was also subjected to the same treatment and their proton conductivity measured under the same conditions. The proton conductivity ( $\sigma$ ) of each membrane was calculated from the impedance data according to the follow equation:

$$\sigma(S \,\mathrm{cm}^{-1}) = \frac{l}{RA} \tag{3}$$

Where  $\sigma$  is the proton conductivity (S cm-1), *l* the membrane thickness (cm), *R* the membrane resistance ( $\Omega$ ), and *A* is the membrane area (cm2).

### **Results and Discussion**

The polyamides and sulfonated copolymers obtained were white rigid fibers. The fiber size increased with decreasing concentration of sulfonated diamine in all the copolymers. The amount of  $CaCl_2$  used in the reaction had a great effect on the polymerization, as it was necessary to add a larger amount (8 to 10% more) of  $CaCl_2$  as the amount of sulfonated diamine increases in the copolymer polymerization reaction. It was also necessary to increase the reaction times described in the literature from 8 a 24 hours, during the synthesis of sulfonated copolyamides. A schematic of the reaction is given in *Figure 1*; The resulting polyamides showed moderated inherent viscosities which decrease with increasing concentration of sulfonated monomer and they are in the range of 0.35-0.19 dL/g in *DMAc* for the copolyamides *HFA-co DABS/ISO* and 0.26-0.14 dL/g for the copolyamides *BFA-co DABS/ISO*. The inherent viscosity is a relative measure of polymer molecular weight, therefore can be considered, the polymer molecular weight decreases when the amount of sulfonated monomer was increased in the copolyamide. This effect had been observed in several sulfonated polymers.



Figure 1. Schematic reaction to obtain the sulfonated copolyamides, BFA-co-DABS/ISO and HFA-co-DABS/ISO. Films of all copolymers elaborated were translucent with a yellowish coloration that intensified as SD increased. The rigidity of the films also increased with increasing sulfonation degree. The thickness of all membrane films was in the range 0.08-0.15 *mm*. The membranes synthesized with monomer *BFA* had a more rigid appearance and they tend to be more brittle than those made from to monomer *HFA*.

The structure of the resulting sulfonated copolyamides was confirmed by *FT IR* and <sup>1</sup>*H NMR* which evidenced the presence of amide and sulfonic groups in the proposed concentrations. *Figure 2* shows the *1H NMR* spectra of (a) *HFAISO* polyamide, and (b) *HFA-co-DABS/ISO* sulfonated copolyamides respectively. The integration area ratio of each proton agrees with the structure of *HFAISO* polyamide, *Figure 1(a)*, and *HFA-co-DABS/ISO* copolyamides, *Figure 1(b)*. Initially there appear two new proton interactions when the sulfonic acid groups are introduced to the polyamide, the peak at 8.95 ppm only appears in the spectra of sulfonated copolymers. This signal corresponds to the ortho proton H<sub>g</sub> respect to the sulfonic acid group, appearing at downfield due to the electron-withdrawing effect of the sulfonic acid group. The aromatic hydrogen atoms H<sub>h</sub> and H<sub>i</sub> near the – SO<sub>3</sub>H group were detected at 8.63 and 7.54 *ppm*, respectively. All the other peaks correspond to other aromatic hydrogen atoms of the chemical structure of the sulfonated copolyamides that are also present in the hompolyamide *HFAISO*. We also observed, for both series that with increasing amount of sulfonated monomer, there is an increase in the intensity of the signal of these protons.

Thermogravimetric analysis showed that the sulfonated copolyamides are stable up to 320 ° C with mass losses of about 12%; Also note that when the amount of sulfonic groups increase, mass loss increases. The homopoliamidas presented stability at temperatures near 460 ° C. All membranes showed higher thermal stability than the *Nafion*  $\otimes$  115 used in this study

As can be seen in *Figure 3*, for the series *HFA-co-DABS/ISO*, membranes with higher sulfonation degree values, tended to have larger water uptake at all temperatures and the water uptakes increase with increasing *SD*. It is also seen that at low temperatures ( $25^{\circ}C$ ) there is a jump in the water uptake between copolymers containing 30 and 40 mol % sulfonic acid groups. This jump is taken as an indication that there is a critical concentration of *-SO3H* groups that given the opening of the structure and vicinity of them allows for an increase in water uptake, as have been reported in other similar polyamides[10]. This behavior was also observed for the sulfonated copolyamides *BFA-co-DABS/ISO*.





Figure 2. 1H NMR of polyamide and sulfonated copolymers.

Figure 3. Water uptake as temperature increase for membranes of HFAISO polyamide and HFA-co-DABS/ISO sulfonated copolyamides.

The proton conductivity,  $\sigma$ , and ion exchange capacity, *IEC* for membranes *HFA-co-DABS/ISO* and *BFA-co-DABS/ISO* at 25 °C is shown in *Figure 4* and *Figure 5*, respectively. *Nafion*® *115* was used for comparison with the membranes synthesized in this work. The membranes obtained from copolyamides showed an increase for *IEC* and proton conductivity,  $\sigma$ , with increasing degree of sulfonation, this is attributed to the increase on water concentration and retention of sulfonated polyamides due to the increased concentration of sulfonic groups, which in turn opens the sites available for ionic exchange in the structure, and increases the possibilities of an enhanced proton transfer capacity. As shown in *Figure 4* and *Figure 5*, an increase in *SD* from 20 to 50 % results in an increase of up to two orders of magnitude in proton conductivity values. These results indicate that it is possible to render proton conductive copolymers based on polyaramides such as those prepared in this work.





Figure 4. Proton conductivity and IEC for membranes of HFAISO polyamide and HFA-co-DABS/ISO sulfonated copolyamides, with increasing sulfonation degree.

Figure 5. Proton conductivity and IEC for membranes of BFAISO polyamide and BFA-co-DABS/ISO sulfonated copolyamides, with increasing sulfonation degree.

### Conclusions

Membranes based on rigid copolyaramides were obtained with increasing degree of sulfonation by direct polycondensation, the rigidity of the films increased with increasing sulfonation degree. The analysis of water uptake, *IEC* and proton conductivity, generally show that they increase with increasing concentration of sulfonated diamine in the copolyamides. The membrane *BFAS55* and *HFAS55* show values of water uptake and *IEC* higher than that of *Nafion*® *115* at room temperature. Proton conductivity values at room temperature obtained with the membrane *BFAS55* and *HFAS55* are in the same order of magnitude as those obtained for *Nafion*® *115*. Overall membranes prepared from *GS* of 50 mol% should be consider good candidates for proton exchange membranes with improved thermal stability as compared to the ones used actually.

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# AN EFFECTIVE PROCEDURE TO OBTAIN MATRIX MIXED MEMBRANES BASED ON POLYSULFONE AND MCM-48 SILICA

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A Matrix Mixed Membrane (MMM) system is a recent alternative to inorganic and polymeric membranes because they combine the superior permeability and selectivity of inorganic membranes with the processability of polymer membranes. Additionally, MMM's are mechanically more resilient than inorganic membranes. Also, these systems have reproducible properties, facile and low cost of fabrication [1].

Preparing MMM's is not exempt from challenges. The low affinity between polymer and inorganic additive can result in the formation of non-selective voids at the polymer-additive interface that decrease the performance of the membrane systems. Another challenge that MMMs could face is partial blockage of the additive pores by polymer chains rendering the additive as a filler [1].

The main of this work is to show a feasible process to prepare MMM's by using polysulfone and MCM-48 silica modificated with 3-Aminopropyl trimethoxysilane (APS). The obtained MMM's were characterized by Scanning Electron Microscopy (SEM), Fourier Transformed Infrared Spectroscopy (FTIR), Thermal Gravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC) and Dynamical Mechanical Analysis (DMA).

The results show the analysis of the interaction between polymer chains and MCM-48 silica particles. Finally, the experimental procedure developed in this research indicates that it was possible to obtain MMM's with MCM-48 silica dispersion into the polymeric matrix with improved mechanical properties of the final composite membranes.

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# AROMATIC POLYAMIDES DENSITY FROM MOLECULAR DYNAMICS SIMULATION

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# Introduction

Molecular dynamics (MD) simulation is a research tool that allows calculating some bulk properties of polymers. Simulation techniques have become widely used to understand the relationships between the molecular structure of amorphous polymer and its properties. Some properties computed by using MD simulations are gas diffusion coefficients, free volume distributions, glass transition temperature and density of polymers. Knowing the density of a polymer should be the first step in the design of new polymers for membrane technology, because it is important regarding packaging. Prathab et al., [1] used condensed-phase optimized potentials for atomistic simulation studies (COMPASS) force field, for the development of a protocol to compute densities of perfluoroalkyl methacrylates. Using this approach, we have attempted a systematic investigation of the densities of a series of aromatic polyamides, in which the structure varies in the pendant group on the diacid monomer. The aromatic polyamides are interesting polymeric materials with application in the membrane science for gas separation. The experimental studies of aromatic polyamides based on 4,4'-hexafluoroisopropylidene diamine (HFA) showed a relationship between the density and the gas transport properties as result of the addition of different concentrations of pendant groups in the diacid monomer [2]. These published densities can be used to validate MD simulation method, which also can be used to compute densities of new aromatic polyamides without having to synthesize them. The seven structures used for this study and its acronyms are given in the figure 1.

# Metodology

All simulations were performed on an hp-Z400 workstation using Material Studio (version 5.5) software package from Accelrys Inc. The simulation of densities were carried out using the DISCOVER package employing the COMPASS force field. For each polymer, the repeating unit was first built and its geometry optimized by energy minimization using the COMPASS force field. Then, the Amorphous Cell module was employed to fold one aromatic polyamide chain (with 5, 10, 15, and 20 repeating units) into a periodic unit cell at 298 K to generate 10 configurations at low density (0.02 g/cm<sup>3</sup>). Then, the configuration with the lowest energy was selected to apply an energy minimization using the method of steepest descent followed by the conjugate gradient method. After minimization, the molecular dynamic (MD) simulations were carried out using NVT (600 and 298 K) and NPT (1000, 30000, 5000, and 1 bar at 50-ps and 298 K) according to the protocol described by Karayiannis et al., [3] in order to obtain an optimized polymer cell. In the last step, a total of 1000-ps NPT MD simulation at 1.0 bar and 298 K was performed to check the density calculation.





**Figure 1**. Structures of aromatic polyamides based on 4,4'-hexafluoroisopropylidene diamine (HFA) utilized in this study.

### **Results and Discussion**

The density results from NPT-MD simulations of HFAISO and HFATERT aromatic polyamides are shown in the figure 2. Compared with the experimental densities, the simulated densities are in good agreement. The density reported for HFAISO and HFATERT are 1.422/1.411 and 1.305/1.304 g/cm<sup>3</sup>, respectively [2,4]. Therefore, these results validate that MD simulation is a relatively effective method to predict densities of aromatic polyamides. On the basis of these data, we employed MD simulations to evaluate densities of aromatic polyamides, which have different pendant groups on the diacid monomer. The calculated density values of aromatic polyamides are given in the table 1. These data show that the density value decrease in the following order: HFAPFB > HFATFM > HFAHIA > HFADHIA > HFAISO > HFATERT > HFATMP. The higher density was obtained in aromatic polyamides with fluorine pendant group. The introduction of this group in side chain of polydimethylsiloxane [5] and perfluoroalkyl methacrylates [1] increased the density value. Interestingly, the density calculation for HFATMP aromatic polyamide was lower.

On the order hand, the aromatic polyamides with hydroxyl pendant groups have been synthesized in our laboratory modifying the diacid monomer. The HFADHIA polyamide is not able to form membranes by solvent casting. Whereas, HFAHIA polyamide was obtained in fibers and its membranes were obtained by solvent casting in dimethylformamide (DMF).



**Figure 2**. NPT-MD simulations for the density of HFAISO and HFATERT aromatic polyamides run to 298 K, pressure 1 bar and 1000 ps.

**Table 1**. Densities computed from NPT-MD simulation for aromatic polyamides based on 4,4'- hexafluoroisopropylidene diamine (HFA).

n-mers	HFAISO	HFAHIA	HFATERT	HFATMP	HFAPFB	HFATFM	HFADHIA
5	1.4152	1.4178	1.2962	1.3027	1.5466	1.4942	1.3921
10	1.4378	1.4341	1.3150	1.2936	1.5188	1.4704	1.4373
15	1.4125	1.4409	1.3266	1.3077	1.5262	1.5045	1.4197
20	1.4028	1.4398	1.3023	1.3197	1.5573	1.4813	1.4334
Average	1.4171	1.4331	1.3100	1.3059	1.5372	1.4876	1.4206
density	$\pm 0.0148$	$\pm 0.0092$	±0.0135	±0.0109	$\pm 0.0178$	±0.0149	±0.0204
$(g/cm^3)$							

At this point, the calculated density data were used to evaluate chain packaging by calculating the fractional free volume (FFV<sup>c</sup>), which was estimated using the following relation: FFV<sup>c</sup> = ( $V_{sp}$ - $1.3V_{\rm vdW}$  VACB)/V<sub>sp</sub>, where V<sub>sp</sub> is the polymer specific volume and V<sub>vdW</sub> is the van der Waals volume of a structural unit, which was calculated using the method, termed atomic and bond contributions of van der Waals volume (VACB) [6]. Moreover, FFV has been also determined using the following relation:  $FFV^{cell} = (V_{Box} - 1.3V_{vdW}^{VACB})/V_{Box}$ , where  $V_{Box}$  is the volume of the optimized polymer cell after minimization protocol employed in MD simulation. These results are shown in the table 2. Both FFV<sup>c</sup> and FFV<sup>cell</sup> values present the following order: HFATMP > HFATERT > HFAHIA > HFATFM > HFAISO > HFAHIA > HFAPFB. Carrera-Figueiras and Aguilar-Vega [2] and Morisato et al., [4] have reported FFV values for HFAISO and HFATERT by using van der Waals volume obtained from Bondi's group contribution method. These results are higher than those obtained in this work. This result can be due to the fact that van der Waals volume ( $V_{vdW}$ ) increments are only valid for groups bonded to carbon. Therefore, the  $V_{vdW}$  values of any non-hydrocarbon molecules obtained by summation of these latter increments are approximated and there may be in error by up 3.32 Å<sup>3</sup>/molecule. It is noteworthy that the simulated results of FFV<sup>cell</sup> revealed that the HFATMP aromatic polyamide has the greater FFV value.

	van der Waals	<b>FFV</b> <sup>c</sup>	FFV <sup>cell</sup>	$T_{\rm g}^{\ \ { m cal}}$	$T_{ m g}$
Polymer	volume	(%)	(%)	(°C)	-
	(Å <sup>3</sup> /molecule)*				
HFAISO	381.00	9.01±0.94	9.32±0.92	295	$294^2, 297^4$
HFAHIA	389.79	$9.00 \pm 0.56$	9.33±0.89		
HFATERT	450.20	11.32±0.92	$11.61 \pm 1.05$	319	$306^2, 315^4$
HFATMP	548.76	12.58±0.72	$12.81 \pm 0.82$		
HFAPFB	516.21	7.92±1.06	$7.90 \pm 0.81$		
HFATFM	556.88	$10.01 \pm 0.90$	10.23±0.89		
HFADHIA	398.59	$10.72 \pm 1.28$	$11.04{\pm}1.47$		
+ G 1 1 1		<b>D</b> 1 <b>G</b> 11 1	<u> </u>		

**Table 2**. Some simulated physical properties of aromatic polyamides.

\*Calculated using Atomic and Bond Contributions of van der Waals Volume (VABC) method [6].

The glass transition temperature  $(T_g)$  of polymeric materials can be determined by plotting FFV versus temperature with NPT-MD simulations and reporting where the slope changes. The figure 3 shows the plot of the FFV<sup>cell</sup> average values of aromatic polyamides against 1000/T [7]. Using these data we calculate the  $T_g$  values for HFAISO and HFATERT aromatic polyamides, which were obtained by the intersection of the two least squares lines. The volume variation of the periodic unit cell was obtained by cooling from 750 K stepwise to 300 K by decrements of 50 K, at each temperature, a constant NPT-MD simulation was conducted to 1000 ps. The results of  $T_g$ -MD simulations obtained for HFAISO and HFATERT are in good agreement with the experimental values of  $T_g$  reported for these polyamides (see Table 2). Therefore, MD simulation is a relatively effective method to predict  $T_g$  of aromatic polyamides studied in this study.



**Figure 3**. Molecular dynamics simulation of glass transition temperature  $(T_g)$  of HFAISO and HFATERT aromatic polyamides.

### Conclusions

In the present study, molecular dynamics (MD) simulation of seven aromatic polyamides with different pendant groups on the diacid moiety were carried out to determine the effect of different side groups on polyamide density and fractional free volume (FFV). Moreover, theoretical data

were validated using experimental values reported for HFAISO and HFATERT. The lower density and higher fractional free volume were observed in the HFATMP after applying a series of NVT and NPT-MD simulations. This polyamide can be synthesized using the HFAHIA aromatic polyamide as precursor.

# Acknowledgements

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SELF-ASSEMBLING NANOMATERIALS AND BLENDS

# STAR POLYETHYLENES VIA ETHYLENE "LIVING" POLYMERIZATION

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I will present, in this communication, our successful synthesis of various star polyethylenes using ethylene "living" polymerization catalyzed with Pd–diimine catalysts via either "core-first" or "arm-first" strategy.

In the "core-first" strategy, we synthesized several multinuclear Pd-diimine catalysts with the nucleus number ranging from 3 to 30 per core, which contain multiple metal centers joined to a common core through their initiating sites. Ethylene "living" polymerization with these multinuclear catalysts leads directly to the synthesis of star polyethylenes with a controllable number of "living" arms. It is demonstrated that the arm number is controlled by changing the nucleus number of the multinuclear catalysts; and the arm length is narrow distributed and is controlled by changing ethylene polymerization time.

In the "arm-first" strategy, we first synthesized various narrow-distributed polyethylenes having various molecular weights and containing an end-capping 2-bromoisobutyryl functionality via ethylene "living" polymerization catalyzed with a functional Pd-diimine catalyst, which uniquely contains a 2-bromoisobutyryl group at its initiating end. The end-capped polyethylenes are then used as macroinitiators for ATRP of divinylbenzene to form star polymers with polyethylene arms and a crosslinked poly(divinylbenzene) core. It is demonstrated that the arm length in these stars is controlled by changing ethylene "living" polymerization time in the first step, and the arm number and core size are controlled by tuning the polymerization parameters in the second ATRP step.

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### NANOCOMPOSITES FORMED FROM POLYOLEFIN-BASED IONOMERS

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The platelets of the clay mineral montmorillonite are  $\sim 1$  nm thick and have rather large lateral dimensions; thus, individual platelets can be very high aspect ratio nanofillers. Montmorillonite can be organically modified by ion-exchange process to make the aluminosilicate layers more hydrophobic and compatible with organic polymers. There has been much interest over the past two decades in making polymer nanocomposites from these organoclays, and our laboratory has been exploring the opportunities of such nanocomposites and the fundamental understanding of their formation and performance. Exfoliation of properly designed organoclays is excellent in polyamides where high degrees of reinforcements can be achieved, but this invariably leads to loss in ductility. On the other hand, exfoliation in polyolefins is generally poor, but there is much interest in finding effective ways of using organoclays in polyolefin systems to achieve enhanced performance. This presentation will give background on organoclays and the issues that affect their exfoliation in polymers. Exfoliation can be significantly improved, relative to what can be achieved in polyethylene or polypropylene, by grafting with maleic anhydride [1] or copolymerization with polar monomers like vinyl acetate [2] or methacrylic acid [3] as previous work from our laboratory Here we explore the opportunities for improved property sets by forming has shown. nanocomposites from Surlyn-type ionomers; these are ethylene-methacrylic acid random copolymers where some fraction of the carboxyl groups have been neutralized with bases to form salts. Ethylene-methacrylic acid copolymers of fixed methacrylic acid content have been neutralized to varying extents to form two series of ionomers; in one the counterion is sodium while in the other it is potassium. Potassium ionomers are of growing interest because they tend to provide better dissipation of static charge, apparently because they sorb more water than do sodium ionomers. This presentation will compare the morphology and properties of nanocomposites formed from these two series of ionomers as a function of the degree of neutralization.

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# ULTRA-STABLE NANOSTRUCTURED POLYMERIC FILMS

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Here we demonstrate that Matrix Assisted Pulsed Laser Evaporation (MAPLE) can be used to fabricate polymer glasses with extraordinarily low densities and simultaneously exceptional thermal and kinetic stability. In addition, these glasses have significantly enhanced glass transition temperatures. Relative to the standard poly(methyl methacrylate) glass formed on cooling at standard rates, glasses prepared by MAPLE can be 40 percent less dense and have 40 K higher glass transition temperatures. Furthermore, the kinetic stability in the glassy-state can be enhanced by 2-orders-of-magnitude. This unique (and unprecedented) combination of properties is a result of the glass morphology, i.e., the glasses are nano-structured. We hypothesize that they are formed by the assembly of spherical-like polymer globules. In essence, we have created what we term "supramolecular structured glasses." The unique set of properties of MAPLE-deposited glasses may make them attractive in technologies where weight and stability are central design issues.
# FUNCTIONAL BLOCK COPOLYMERS AS POLYMERIC DISPERSING AGENTS FOR NANOMATERIALS

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Macro-M is a company that specializes in the synthesis of block copolymers containing reactive functional groups in one of their blocks. These materials are used as compatibilizers for polymer blends and also as dispersants for several particle-polymer systems. The present talk will cover the use of a series of block copolymers synthesized via controlled radical polymerization (CRP) to enhance the dispersion and or exfoliation of nanoclays in thermoplastic or thermoset resins. The block copolymers can either be used with existing, commercially-available clays, or it can be designed as an intercalant in producing a clay nanocomposite material. The CRP technique allows fine tuning the molecular weight, the amount of functional groups and the composition of blocks, in order to obtain an optimal performance between nanofiller and the polymer. A selection of their performance as compatibilizers in several polymer-clay systems will be addressed, and a correlation of the mechanical properties with the intrinsic variables of the compatibilizer (Mn, composition, etc.) will be discussed

# MICRO AND NANO LAYERED POLYMERIC SYSTEMS BY FORCED ASSEMBLY

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In recent years, new synthetic approaches have been used to develop macromolecular architectures that "self-assemble" into nano-scale morphologies. This lecture addresses another approach - the "forced-assembly" of synthetic polymers by continuous nanolayer coextrusion. Films can readily be created with thousands of layers containing two or more alternating polymers using a multilayer coextrusion system. Layer thicknesses have been made in the range of several microns down to less than ten nanometers by varying the number of layers and the layer composition.

Nanolayered films are of interest because of a potential for developing materials systems with novel mechanical, transport, electrical and optical properties. Since the radius of gyration of macromolecules can readily exceed the nanolayer thickness, the surrounding layers can be used to impart dimensional constraint or confinement at the molecular level. The novel effects that accompany a decrease in layer thickness from the microscale to the nanoscale have been demonstrated for a number of unique systems including polymer interphase materials, polymer interdiffusion, confined crystallization for high barrier applications, multilayered films for dielectric and capacitor applications and graded index lens (GRIN) systems inspired from biomimetics.

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# SELF-ASSEMBLY OF SILICON-CONTAINING BLOCK COPOLYMERS FOR LITHOGRAPHY APPLICATIONS

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The need to overcome feature-size limitations in conventional lithography has led to the development of new patterning techniques using block copolymer templates. Ideal block copolymer systems for these applications have high etch contrast between blocks to promote good feature resolution and high segment-segment interaction parameters (or chi-parameters) to achieve small features. Etch resistance is promoted in polymers if they contain large amounts of silicon such that they form a robust oxide mask during reactive ion etching with oxygen. To achieve etch contrast in block copolymers, these silicon-containing polymers can be incorporated into a block copolymer where the adjacent block is a hydrocarbon and etches easily. It is also observed that, in some cases, incorporating silicon into one of the blocks increases the chi parameter compared to similar silicon-deficient block copolymers. Here we will present several new block copolymer systems exhibiting BCC sphere and hexagonal packed cylinder morphologies in bulk and thin films that incorporate fast-etching hydrocarbon blocks coupled to a glassy silicon-containing polymer. The silicon-containing block provides sufficient etch resistance to achieve robust patterns in thin films in addition to promoting high chi parameters which enables cylinder and sphere diameters as small as 5 nm.

# SYNTESIS AND CHARACTERIZATION OF A CHITOSAN-GOLD NANOCOMPOSITE FOR BIOSENSOR APLICATIONS

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Chitosan-gold nanoparticles (CS/AunP's) is an attractive biocomposite because of its great potential in biomedicine as biosensor for detection of protein, fetoprotein, DNA glucose, heavy metals etc. Recent literature reports electrochemical biosensors based on CS/AunP's nanocomposites in which biological binding events are converted into useful electrical signals. To further the applications of such bionsensors, the conductivity mechanism of CS/AunP's nanocomposites needs to be addressed. Due to above the aim of this work is to synthesize CS/Au nP's nanocomposites and to investigate the influence of gold nanoparticles concentration and dimension on its structure, conductivity and relaxation properties.

CS/AunP's composites have been synthesized by reduction of HAuCl<sub>4</sub> with sodium citrate (SC) in chitosan solution. Concentration and size of gold nanoparticles have been controlled by varying stoichiometric molar concentrations of HAuCl<sub>4</sub> and SC. Biocomposites with Au nP's concentration between 0-3 wt.% have been successfully synthesized and structurally characterized. Typical dimensions of AunP's are in the 10-16 nm range.

Our results suggest a strong temperature-dependence on the conductivity of the nanocomposite and activation energy on the HAuCl<sub>4</sub> and SC concentration. Based upon a comprehensive DMA and dielectric spectroscopy analyses, a glass transition temperature is observed and it is dependent on AunP's concentration and dimension. Finally, a plausible mechanism of interaction between AunP's and chitosan matrix and its influence on conductivity mechanism have been proposed.

# SYNTHESIS OF POLYMER HYBRID NANOCOMPOSITES USING GREEN CHEMISTRY.

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The development of polymer nanocomposites has been focused on their production, and possible applications [1]. One of the new trends in the synthesis of nanocomposites is the production of nanohybrids, which consist of covalent reaction between nanoparticles and polymer molecules [2]. This hybridization can improve the compatibility and dispersion of nanoparticles in the polymer, thus reducing the toxicity of nanomaterials by preventing the nanoparticles exposure to the environment.

This communication describes the production of hybrid nanocomposite of nylon-6/multi-wall carbon nanotube (MWCNTs), by using green chemistry processes in its manufacture: ultrasound for disagglomeration of nanotubes and microwave radiation for the synthesis of nanohybrids.

Using these green chemistry processes hybrid nanocomposites were produced, having an electrical conductivity of 7.85 x  $10^{-10}$  to 3.13 x  $10^{-5}$  S/cm. In the case of the hybrid nanotubes that were extracted from the hybrid nanocomposites, these form a film with a conductivity of 1.4 x  $10^{-2}$  to 3.4 x  $10^{-1}$  S/cm.

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# SYNTHESIS AND CHARACTERIZATION OF IONOGENIC GRAPHENE OXIDES FOR THE GENERATION OF NEW FUNCTIONALIZED GRAPHENE OXIDE POLYMERS AND MACROMOLECULES

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#### Abstract

The chemical surface modification of graphene and graphene oxides is a burgeoning area of investigation. Not only does it provide an effective springboard for the chemical management of graphene materials and their exfoliation to one-atom thick sheets, it also provides for the design and control of the physical properties of these materials for present and future practical applications. Chemically modified graphene and graphene oxides are expected to facilitate further understanding of the chemistry and physics of graphene materials in general, and contribute to the formation and further understanding of advanced hybrid graphene and graphene oxide polymer nanocomposites [1,2]. The preparation and characterization of new ionic forms of graphene oxide (GO) was prepared by a modified Hummers method and functionalized to form cationic and anionic species. The former were prepared via nucleophilic substitution of alkyl amines at the epoxy and hydroxyl groups on the graphene oxide sheets consist of quaternary ammonium ion substituted GO, GO<sup>+</sup>, with chloride or iodide as the counter ion and sulfonated GO, GO<sup>-</sup>, with hydrogen, sodium, barium or tetraphenyl phosphonium as the counter ion. The addition reaction between GO<sup>+</sup> and GO<sup>-</sup> in aqueous solution was also investigated. Materials were characterized by XRD, FT-IR, Raman, STEM, TEM, TGA, EDAX and AA/ICP.

#### Introduction

Graphene Oxide (GO) is a material consisting of carbon, oxygen, and hydrogen in variable ratios that may be obtained by treating graphite with strong oxidizers. When completely exfoliated, GO is a two-dimensional sheet of  $sp^2$  and  $sp^3$  hybridized carbon atoms, basically one atom thick. Upon chemical reduction, for example, GO may be reduced to graphene (G), which, in its purest form, is defect free and consists only of  $sp^2$  hybridized carbon with no bonded oxygen or peripherally bonded carbon atoms. The remarkable physical properties of asymmetric graphene, such as its extraordinary high intrinsic carrier mobility, tunable band gap and quantum electronic transport, have stimulated interest not only in new fundamental science, but also in applications such as electronics, optoelectronics, and biological sensors [1,2]. The understanding of the chemistry of graphene and its oxides lags far behind that of its physics and offers vast exploratory potential for the understanding and development of new carbon-containing materials and their applications. For example, GO has been subject to covalent modification with polymers resulting in new hybrid graphene/polymer nanocomposites, such as in styrene and isoprene matrices [3], polyelectrolyte multilayers [4], graphene-graphdiynes and conjugated macromolecules for solar cell devices [5] and systems discussed in references [2,6]. For excellent reviews of the emerging chemistry of graphene and its oxide, see for example, Park and Ruoff [7], Drever, at al. [8] and Si, et al. [9]. The current work focuses on the preparation and characterization of ionically functionalized graphene oxides because of their valuable scientific and technological potential to interact with societally important amphiphilic and ionogenic polymers to create optimally dispersed graphene and graphene oxide polymer composites by, for example, addition reactions. Graphene-based polymer composites and polymer graphene interactions have only recently begun to be investigated [10,11]. In the approach described herein, the optimal dispersion of GO, and ultimately graphene, is augmented by the structure and composition of the matrix or host polymer. Moreover, the ionic functionality of GO enhances dispersibility in select solvents for further fabrication of the graphenes into technologically usable materials, Second US-Mexico Meeting "Advanced Polymer Science" and XXIV SPM National Congress

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particularly flexible plastics, polymers and elastomers.

# Experimental

# **Graphene Oxide**

Graphite powder from Aldrich was pre-oxidized using  $H_2SO_4$ ,  $K_2S_2O_8$ , and  $P_2O_5$  by the procedure of Kovtyukhova, et al. [12]. The preoxidized graphite (2 g) was then subjected to the Hummers and Offeman procedure [13] and put into cold (0°C) concentrated  $H_2SO_4$  (46 mL). KMnO<sub>4</sub> (6 g) was added gradually with stirring and cooling to keep the reaction mixture form reaching 20°C. The mixture was then stirred at 35°C for 2 h, after which distilled water (92 mL) was added. In 15 min, the reaction was terminated by the addition of a large amount of distilled water (280 mL) and 30%  $H_2O_2$  solution (5 mL), after which the color of the mixture changed to bright yellow. The mixture was filtered and washed with a 1:10 HCl/water solution (200 mL) in order to remove metal ions, then washed with water until neutral pH. The resulting GO dispersion was suspended in a mixture of ethanol and water to further exfoliate the GO through ultra-sonication for 1 h and then dried at 80°C.

# Preparation of quaternary ammonim ion functionalized graphene oxide

100 mg of GO was dispersed in 10 mL of water, followed by the addition of 300 mg of methylamine in 10 mL of ethanol. The GO solid swelled instantly upon addition of the amine solution. Mixtures were allowed to stir for 20 h at room temperature before isolation of the resulting derivative. This procedure was repeated several times to prepare one gram of sample. 500 mg of GO amine were then dispersed in 25 mL of N-methyl-2-pyrrolidone during 12 h at room temperature. 65 mg of NaOH and 23 mmol of CH<sub>3</sub>I were added to the dispersion. The reaction was carried out with stirring for 12 h at 50°C after which acetone was added to precipitate the desired product shown schematically in Figure 1. The methyl iodide used in the reaction provided iodide as the counter ion. The cation functionalized GO with chloride ion was prepared by addition of 0.01N HCl solution to a water dispersion of 500 mg the GO amine, stirring for 2 h after which the precipitate was washed to neutral pH and dried at 100°C.

# Preparation of the sulfonate ion functionalized graphene oxide

The sulfonated form of GO was prepared according to Si and Samulsk using an aryl diazonium salt [14]. The cationic and anionic functionalized graphene oxide materials are illustrated in Figure 1 of reference [4].

Addition reactions between  $GO^+$ ,  $GO^-$  and polystyrene sulfonate (PSS) in water solution Cationic (80 mg) and anionic (50 mg) GO, or PSS, were previously dispersed in DI water, then sonicated for 30 min and shaken for 12 hr. The precipitates were collected by centrifugation and dispersed in water at least three times, dried at 40°C and finally at 100°C for 24 hr.

# **Results and Discussions**

Graphene oxide was prepared by a modified Hummer's method followed by subsequent amine insertion at the GO epoxy groups to form the aminated species. The resulting N-alkyl graphene oxide was quaternized using methyl chloride or iodide. The sulfonted form of GO resulted from the reduction of GO that was reacted with  $NH_2C_6H_4SO_3HH_2O$ . All prepared species were used in exfoliated form; STEM images for GO, quaternary ammonium GO<sup>+</sup> and sulfonate GO<sup>-</sup> are presented in Figures 1a, b and c, respectively.



Figure 1. STEM images (LEI mode) of (a) GO; (b) GO<sup>+</sup> (with iodide); (c) GO<sup>-</sup> (with H<sup>+</sup>).

In the FT-IR ATR spectra of graphene oxide and its derivatives there exist three characteristic peaks of graphene oxide: a strong and broad absorption at 3400 cm<sup>-1</sup> due to O-H stretching vibrations and the peaks at1706 and1210 cm<sup>-1</sup> ascribed to the C=O stretching vibrations. As the modification of graphene oxide proceeded, the intensities of amine and methyl peaks increased. Although marked differences were not observed in the IR spectra for the quaternized ammonium graphene oxide, the intensities of the peaks around 1460 and 705 cm<sup>-1</sup> (methyl groups) increased with addition of CH<sub>3</sub>I. Elemental analysis of the cation revealed a minimum of 3% N with higher aminations more prevalent. Raman data for GO: 1350 and 1594 cm<sup>-1</sup> for D and G, respectively. G band for GO-cation (I<sup>-</sup>), GO-anion (H<sup>+</sup>) and [GO+][GO-]: 1597, 1602, and 1596 cm<sup>-1</sup>, respectively. D bands for respective species all close to or just slightly higher than 1350 cm<sup>-1</sup>.

The XRD patterns of GO, aminated GO, and its cationic forms are shown in Figure 2a. GO shows a sharp peak corresponding to the literature c-axis spacing of 7.44 Å; the layer-to-layer distance in GO can be strongly influenced by intercalated H<sub>2</sub>O. When amine was inserted in the GO sheets, the layer-to-layer distance increased to 8.05 Å. For the dried cationic forms, the layer-to-layer distance increased from 7.30 to 8.53 Å for the chloride and iodide species, respectively. XRD patterns for the anionic species of GO are presented in Figure 2b. While the protonated species shows relatively sharp peaks, the precipitates formed by exchange with aqueous chloride solutions of Ba<sup>2+</sup> and tetraphenylphosphonium ion (TTP<sup>+</sup>) show broader peaks, perhaps suggesting broad distributions in layer-to-layer distances, sheet foldings and sizes and so on for the barium species. A bit more structure in the XRD is seen for the TTP precipitate, which might be expected to form more structured species due to the presumed hydrophobic coating imparted to the GO, thus possibly diminishing interactions between the [TTP-GO-TTP] entities.

Finally, XRD data for the resulting addition products formed between the GO cation and GO anion and between the GO cation and polystyrene sulfonate (PSS) are shown in Figure 3c, with the patterns for GO and its cation and anion included for comparison. The combination of the reactants in both cases leads to a black, homogeneous precipitate, which, in the latter case, can form films. The patterns for both products are clearly different from those of the starting materials and suggest a purity of 90% or greater. XRD data for the latter shows that

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the GO cation and PSS combine to form an apparently amorphous material in which the GO cations are presumably dispersed in a matrix of the sulfonated polystyrene. Interactions at the ionic level for the latter are schematically illustrated in Figure 3a. In the former case, the black precipitate resulting from the mixture of approximately equal masses of cation and anion, again shows an X-ray powder pattern different form that of either of its constituents and suggests a purity of 90% or greater. In this case, however, some order appears as well as disorder as may result from size and fold differences in the GO sheets as well as from other sources. A possible interaction between the ions at the atomic level is schematically shown in Fig 3b. The sheet-like nature of the product is shown in the TEM image in Figure 4. Further HRTEM analysis is in progress.



Figures 2a, b and c. XRD patterns of GO, GO-amine and GO ionic derivatives as described in the text.



Figure 3. Possible ionic interactions in: (a) [GO<sup>+</sup>][ PSS<sup>-</sup>] and (b) [GO<sup>+</sup>][GO<sup>-</sup>].

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Figure 4. TEM (left) and HRTEM (right) images: aqueous addition product between GO<sup>+</sup> and GO<sup>-</sup>.

# Conclusions

Exfoliated graphene oxide (GO) sheets were successfully functionalized with quaternary ammonium groups by nucleophilic substitution of amines on the GO –OH and C-O-C groups to form the cation functionalized graphene oxide, GO<sup>+</sup>, with chloride and iodide as counter ions. Similarly, GO sheets were successfully functionalized with sulfonate ions using an aryl diazonium salt. Counter ions for the latter included H<sup>+</sup>, Ba<sup>2+</sup> and tetraphenylphosphonium ions. IR and XRD data confirm the structures and are consistent with size and/or stearic effects of the different counter ions on the layerto-layer spacings between the GO sheets. Exfoliation and sheet structure of the species were confirmed by aqueous dispersibility and 'solubility' and by STEM and TEM data. Reaction products between the functionalized GO cations and anions resulted in a black precipitate with an XRD pattern different from that of either starting material. The addition reaction between the GO cation and polystyrene sulfonate resulted in a black, homogeneous amorphous product by X-ray analysis and in one that could form films. The two starting materials were not present by XRD; the product could not be separated into its components by extraction. Data and observations presented herein support the hypothesis of using ionogenic graphene oxides for the preparation of new functionalized graphene oxide polymers, macromolecules and GO polymer nanocomposites. The proposed structure for the GO polymer, [GO<sup>+</sup>][GO<sup>-</sup>], can allow for controlled interlayer spacing and an entirely new layered structure for intercalation. Further elucidation of the chemistry and properties of these materials is underway along with their potential in producing new materials with other macromolecular and polymeric systems.

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# EFFECT OF DICUMYL PEROXIDE (DCP) CONCENTRATION ON THE REACTIVE BLENDING OF POLYPROPYLENE (PP) AND ETHYLENE VINYL ACETATE (EVA)

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We studied the effect of DCP concentration as an initiator in the molten state to create reactive blends of PP and EVA for the functionalization of polypropylene [1]. The reaction mechanism for PP-EVA reactive blending has been only reported in the solid state using radiation as reaction initiator [2]. In the present work, the reactive blends were prepared under the equal weight concentration of both polymers to reduce parallel reactions as  $\beta$ -scission of PP and crosslinking of EVA. Three different DCP concentrations were used. The morphology and thermal and mechanical properties of PP-EVA samples were also studied as a function of the DCP concentration.

The reaction mechanism analysis showed that with increased DCP concentration, the hydrogen extraction reaction increased in both polymers. The main propagation reactions were determined to be the PP  $\beta$ -scission and EVA deacetylation. It was also observed that the most important termination reaction was the chemical linking between PP and EVA which was dependent on DCP concentration.

The iPP-EVA reactive blends obtained by above reactions, showed an increase in compatibility between the phases compare to the blends obtained without use of DCP. We also found decrease in mechanical properties (DMA and Tensile) when the DCP concentration was increased. The thermal properties were not substantially modified.

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# SYNTHESIS AND CHARACTERIZATION OF POLY(3-HEXYL THIOPHENE) (P3HT) THIN FILMS AND THEIR APPLICATIONS TO SOLAR CELL WITH SEMICONDUCTOR NANOPARTICLES

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Poli (3-hexiltiofeno) (P3HT) is a p-type polymer semiconductor material which is currently employed in organic solar cells. P3HT has relatively high mobility compared with other polymer semiconductors, is soluble in several solvents and its processing is very easy. Among the different configurations used in an organic heterojunction solar cell, one of the most studied configuration is a mixture of a soluble conjugated p-type polymer and n-type inorganic semiconductor nanoparticles that are deposited in a solution. The p-type polymer-semiconductor material work as a donor and inorganic nanoparticles work as acceptor. This blend of conducting polymers and inorganic nanoparticles are promising materials in photovoltaic devices. In this work we have deposited P3HT thin films by spin coating and cured at several times and temperatures in the range 60-210 °C. We report here the structural and electrical characterization of the films as a function of the curing parameters. Furthermore, we applied the P3HT films to the fabrication of solar cells by embedding CdS nanoparticles in the polymeric matrix. We also report here the electrical analysis of the obtained P3HT-based solar cell devices.

# PET NANOSTRUCTURED WITH MORDENITE DOPED WITH COPPER FOR GENERATING ELECTRICAL CONDUCTIVITY

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Nanocomposite polymer fibers of polyethylene terephthalate (PET) containing 2 % w/w mordenite, with metallic copper on the surface at different concentrations, were studied. Samples were characterized using WAXD, SAXS, SEM, physisorption and conductivity tests in order to determine their property/structure relationship. The main results indicated that fibers containing mordenite and metallic copper had an increase of four orders of magnitude in conductivity. SEM morphological changes were the basis to explain the results. Corresponding mechanical tests indicated that the fibers tenacity was improved due to an increase of Young's modulus. The studied fibers also displayed lower elongation at break due to the incorporation of mordenite into the polymeric matrix. WAXD studies showed that the nanostructured fibers maintained the characteristic PET crystalline structure, however, it was determined that crystallinity decreased due to the extrusion process. DSC analyses indicated that mordenite was also a nucleating agent.

#### Introduction

Polymers are insulating materials; therefore, a great deal of research has recently been made in order to transform them into conductive polymers. Some of the latest innovations have involved doping of the polymer and the incorporation of a metal conductor [1] or carbon nanotubes [2]. Some studies have also been made in order to improve the mechanical properties through, for example, the inclusion of reinforcements, such as clays [3], silica [4] and carbon nanotubes [2]. In any case, the improvement of the indicated properties requires good additive dispersion into the polymeric matrix. Therefore, the main objective of this study was to obtain a well dispersed PET/mordenite-Cu nanocomposite and determine the main mechanical and electrical properties of the fiber products.

#### **Experimental Section**

Copper adsorption was made on the surface of synthetic mordenite, through incipient wetness impregnation, followed by oxygen calcination and hydrogen reduction. The resulting material was incorporated into the polymeric matrix of PET by extrusion in order to obtain PET nanostructured fibers. The resultant fibers were subject to conductivity studies, wide angle X-ray diffraction (WAXD), small-angle X-ray scattering (SAXS), scanning electron microscopy (SEM), differential scanning calorimetry (DSC) and mechanical property measurements.

The synthetic mordenite used in this study was purchased from Zeolyst International Co. and had a pore diameter of 10 Å. PET 7352 was purchased from Eastman Kodak Co. in the form of pellets. The cupric nitrate was from Fermont Co., and oxygen, nitrogen, argon and hydrogen of high purity were from Infra S. A.

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### Doping and characterization of zeolites

The studied mordenite was first impregnated via incipient wetness using a solution of cupric nitrate. Once dried, the calcinations process was carried out in an oven using nitrogen flow and heating ramps from 100 to 500 ° C. The material was ultimately maintained at 500 ° C for one hour in oxygen flow with the purpose to remove nitrates and obtain copper oxide. The reduction of copper to metallic state was performed in a differential flow reactor which was heated from 25 to 200 ° C, remaining there for two hours before cooling at room temperature. In the last step, a mixed flow of 10% v/v hydrogen and 90% v/v argon at a rate of 100 ml / min was introduced in the reactor and the material was heated at a rate of 10 ° C / min up to 600 ° C, where it remained 10 minutes. The studied mordenite with metal copper on the surface was analyzed in pellet form by WAXD using a PANalytical diffractometer XPert PRO, and SAXS using a Bruker, Nanostar equipment. Once the presence of metallic copper was determined, the volumetric electrical resistivity (Rv) of pellets was measured in two points using the Cabot Method (ASTM D-4496). Before physisorption analysis, it was necessary a heat pretreatment at 250°C, samples were gold covered for SEM determinations.

#### Nanocomposites Preparation

The method of nanocomposite preparation first involved drying the material at 100  $^{\circ}$  C for 2 hours, then the PET and sieved mordenite were vigorously agitated in test tubes and then fed into an extrusion system. The extruder used to generate fibers was a mini laboratory extruder Dynisco LME-120 operated at a temperature of 280  $^{\circ}$  C in the mixing chamber and 270  $^{\circ}$  C in the die, a residence time of 35 seconds and a speed of 40 rpm were used for this purpose.

#### **Results and Discussion**

In order to obtain the textural properties of mordenite and their changes with the addition of copper on the surface, physisorption analysis were first made. Table 1 shows the experimental results, where it is shown that mordenite has a high adsorption capacity and a large surface area, together with porosity in the range of micropores.

	Pure Mordenite	Mordenite with 5% wt of reduced copper	Mordenite with 20% wt of reduced copper
Surface area	404 m <sup>2</sup> /g	366 m <sup>2</sup> /g	298 m²/g
Meso and macropores area	128 m²/g	123 m <sup>2</sup> /g	114 m <sup>2</sup> /g
Micropores area	277 m²/g	243 m <sup>2</sup> /g	185 m <sup>2</sup> /g
Micropores volume	0.1306 cm <sup>3</sup> /g	$0.1080 \text{ cm}^3/\text{g}$	$0.0496 \text{ cm}^3/\text{g}$
Pore diameter	10*10 <sup>-10</sup> m	10*10 <sup>-10</sup> m	10*10 <sup>-10</sup> m
CONDUCTIVITY	1.86 * 10 <sup>-3</sup> S/cm	$8.60 * 10^{-1}$ S/cm	$1.70 * 10^2$ S/cm

Table 1. Physisorption and conductivity data for neat and modified mordenite.

In the previous results, a decrease in surface area of zeolite is observed in direct proportion with the amount of deposited cooper. There is also a decrease of the porous area, although the one related to the micropores decreases in larger proportion. Therefore, the results indicate that copper deposition mainly occurred covering the small pores. Due to the reported sizes of the copper cumulus  $(60x10^{-6} \text{ m } [5])$ , it is proposed that some copper particles block several pores, which are about  $10x10^{-10}$  m in size, as a consequence, mordenite experiences a micropores volume decrease. The highest percentage of copper deposited was 20%, since this is the limit of acceptance of the solution by

zeolite in the method of impregnation. The purpose to saturate zeolite with metallic copper in this work was to achieve the highest possible electrical conductivity.

As indicated before, in order to measure the volumetric electrical resistivity in two points, the method of Cabot was used. The results in Table 1 show that the incorporation of copper in the reduced state increases in five orders of magnitude the products conductivity. The results are in the range of conductors, placing these PET composites as ones with conductive properties.

The samples morphology was sequentially characterized beginning with WAXD studies been the purpose to determine potential mordenite changes and the metallic copper presence. SAXS studies were made to determine the nature of copper deposition.

Figure 1 shows the diffraction pattern of pure mordenite, which is in coincidence with the reported structure [6]. The presence of metallic copper is also detected through three main planar reflections  $(2\theta = 45^{\circ}, 51^{\circ} \text{ and } 74^{\circ})$ . The reference pattern of a sample with copper oxide is also shown. From the results, it was determined that the original structure of the zeolite was maintained, this in spite of the heat treatments to which the corresponding samples were subjected. The SAXS results indicate the lack of periodicity in mordenite since there is not a reference ring. Therefore, there is only a circular halo. However, there was a difference in intensities due to the presence of higher copper concentration in the system. The results indicate that neither mordenite nor metallic cooper have periodicity in this composite system. Although the presence of copper, most probably because of its spherical appearance (see bright points in the inset), makes only an overall intensity contribution.



**Figure 1.** 1) X-ray diffraction results, 2) X-ray scattering results and 3) SEM image of: a) neat mordenite, b) mordenite with 5% wt of oxidized copper, c) mordenite with 5% wt of reduced copper and d) mordenite with 20% wt of reduced copper.

The diffraction patterns in Figure 2 are evidence that the PET fibers are rather amorphous [7]. This is because there are not well-defined diffraction peaks, although there is a sharper definition of the main amorphous peak together with the tendency to disappear the first amorphous hump. Other than these effects, the mordenite reflections appear at  $2\theta = 8^{\circ}$  y 9° and those related to copper at  $2\theta = 45^{\circ}$ ,  $51^{\circ}$  and  $74^{\circ}$ .

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**Figure 2.** X-ray diffraction patterns and conductivity data for fibers of: a) PET homopolymer, b) PET with 2% of zeolite with 5% reduced Cu c) PET with 2% of zeolite with 20% of reduced Cu.

Corresponding DSC studies of the thermal evolution of products (not shown here) allowed determining three characteristic melting endotherms during scanning after the isothermal crystallization process. It was in addition observed that increasing the crystallization temperature would lead to an increase in the first melting endotherm and contrastingly increasing mordenite content, would lead to a decrease of the second melting endotherm, causing a decrease in crystallization, analyses of non-isothermal crystallization indicated that mordenite acts as heterogeneous nucleating agent.

The samples mechanical properties are summarized in Table 2, where in general it can be observed that the incorporation of zeolite results in improved mechanical properties of the fiber. For example, the results show that Young's Modulus and strain at break increased from 0.94 to 1.4 (N/Tex) and from 0.02 to 0.03 (N) respectively, while the maximum strain percentage decreased.

FIBER	PET	PET + 1% of	PET + 2% of	PET + 2% of	PET + 2% of
		zeolite with 20%	zeolite with 20%	zeolite with 5%	zeolite with 20%
		of reduced Cu	of oxidized Cu	of reduced Cu	of reduced Cu
Tension at break (N/Tex)	0.02	0.03	0.03	0.03	0.04
% of Maximum deformation	6.27	4.00	3.80	3.80	3.15
Energy (J)	0.07	0.04	0.04	0.04	0.03
Young's Modulus (N/Tex)	0.94	1.4	1.50	1.46	1.49

Table 2. Mechanical properties of fibers analyzed.

As for the mechanism of species evolution, the SEM micrographs in Figure 3 show that mordenites tend to cluster into a fibril shape, following ramified patterns. It should be pointed out that the overall trajectory orientation shown in the micrographs correspond to the direction of fiber and that the selected fiber sections are only part of the total diameter of the polymer fiber. Therefore, according to the previous results, and comparing these with the morphology in Figure 3, we can deduce that this morphology favors the conduction of electricity. This is because copper in the zeolite clusters have a greater chance of contact with adjacent clusters.



Figure 3. SEM micrographs of PET fibers with: 2% mordenite with a) 5% of copper oxide, b) 5% reduced copper c) 20% reduced copper.

#### Conclusions

A new nanometric semiconductive PET/mordenite-copper system has been prepared and characterized. The effects of preparation indicated that some copper particles blocked pores; as a consequence, mordenite experienced a microporous volume decrease.

The characterization results indicated the lack of periodicity both in mordenite and metallic cooper. The presence of spherical copper clusters only made an overall intensity contribution.

In general terms, mordenite incorporation improved the Young modulus of fibers.

Mordenites tended to cluster into a fibril shape, following ramified patterns. This morphology was argued to favor the conduction of electricity, because in this form copper clusters have a greater chance of contact with adjacent clusters

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# ANILINIUM SALTS AS SURFMERS IN THE SYNTHESIS OF ELECTRICALLY CONDUCTING POLYANILINE BASED COMPOSITES

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# Abstract

Anilinium dodecyl sulfate (DS-AN) was obtained from aniline and sodium dodecyl sulfate (SDS). Critic micellar concentration (cmc) of the salt was determined by electrical conductimetry. This technique showed that the change of counterion, sodium by anilinium, induced the reduction of cmc with respect to their conventional counterpart, SDS. Afterwards, DS-AN was used as reactive surfactant (surfmer) in the synthesis of polystyrene / polyaniline core-shell conductive composites. The latexes obtained were stable, which indicated that DS-AN followed the mechanism implicated in traditional emulsion polymerization. Polyaniline synthesis was successfully performed by adding more DS-AN as the monomer and APS as the oxidizing agent, no acid addition was required in this procedure. The composite presented conductivities in the order of  $10^{-4}$  to  $10^{-3}$  S/cm.

# Introduction

Polymerizable surfactants, also known as surfmers, are a special class of surfactants. These compounds are especially attractive because, besides of acting as conventional emulsifiers, they have the ability to link covalently to the surface of latex particles [1]. This feature avoids surfactant desorption from the polymer particles and improves resistance to freezing and high shearing of the latex [2]. Most surfmers are susceptible of homo and copolymerization [3]; however, maleic surfmers are only able to copolymerize [4].

In this work we are reporting results of anilinium dodecyl sulfate (DS-AN) salt used as surfmer in the synthesis of core-shell composites obtained in two steps. In this case, functionality lies on the anilinium group and not on a polymerizable carbon-carbon double bond as in traditional surfmers; neither its reactive activity develops within the oily phase of some emulsion system, as usually reported [5]. These features make a big difference of this anfifile with respect to the traditional concept of surfmer.

# Experimental

# **DS-AN** synthesis

DS-AN salt was synthesized as follows: First, the salt of anilinium hydrochloride was obtained by reacting aniline and hydrochloric in aqueous medium. Next, an aqueous solution of sodium dodecyl sulfate (SDS) was mixed with the salt of anilinium hydrochloride. Product purification was performed by saturating an aqueous solution at ~50 °C.

# **Critic micellar concentration**

Critic micellar concentration (cmc) of DS-AN was determined by electrical conductimetry. The procedure was as follows: An aqueous concentrated solution of the salts was prepared at laboratory conditions. 100 mL of demineralized water with electrical conductivity of ~1.8 S/cm was loaded in a glass vessel and tempered at 27 °C. The cell of the conductivity meter was fixed 1 cm above the vessel bottom. Progressive additions of 1 mL each time of the salt solution were achieved. The evaluation consisted in measuring the increase of electrical conductivity as function of salt concentration. Gentle magnetic stirring was used to homogenize the solution.

# **Emulsion polymerization**

Styrene emulsion polymerization, was performed as follows: First, aqueous solution of DS-AN was loaded into the reactor and let to stabilize for 20 min at 70 °C in the presence of nitrogen. Afterwards, initiator V-50 was loaded to the reactor and the solution was let for 5 min more. Next, the emulsion was prepared by injecting the styrene monomer into the reactor with vigorous stirring. The relationship monomer to water was 20 to 80 (wt/wt). All polymerizations were performed at 70 °C, stirring of 300 rpm and let for 180 min with permanent flux of nitrogen. Once polymerizations finished the latexes were let cool and kept into covered vessels. Series of samples were taken along the polymerization to determine kinetics.

# **Oxidative polymerization**

PAni shell synthesis, as the second step, was carried out as follows: First, 50 mL of polystyrene latex was loaded into a glass vessel. In a separate container an aqueous solution of DS-AN was prepared at ~50 °C and magnetic stirring. Afterwards, the solution and the latex were mixed together keeping magnetic stirring and temperature for 2 h in order to allow the salt to absorb onto the polymer particles surface. After this time, the system was let cool to room conditions. Finally, an aqueous solution of ammonium persulfate (APS) was poured to start PAni synthesis. Oxidative polymerization was carried out at laboratory conditions and allowed for 24 h.

# **Results and discussion**

# CMC

The curves of electrical conductivity (S/cm) versus surfactant concentration (mol/L) of SDS and DS-AN, are shown in Figure 1. The change in the slop for SDS was at 8.1 mmol/L. This value agreed well with literature, which also let us to validate our experimental procedure [6]. Of course, variations can be found in the values of the cmc depending, for example, on the surfactant purity. In special ionic impurities can promote changes in this value, since they can alter solution conductivity. In the case of DS-AN the slop changed at 3.1 mmol/L; that is, 2.6 times lower than the cmc of SDS. This change indicated that the effect of changing countercation was very important. The effect of changing inorganic counterion by organic counterion, in conventional surfactants, has been studied. As examples, we can comment that Li et al. [7] reported the effect of changing alkyl radical length of decylammonium dicarboxylate or monocarboxylate surfactants. They found that depending on the n-alkanoate radical the cmc reduced as function of length. However, the most important effect was observed with the monocarboxylated due to the easier incorporation of the alkyl chain into the micellar aggregate. Gamboa et al. [8] studied the effect of changing Cl- or Br- anions by Tosylate anion in cetyltimethylammonium surfactants. They reported the reduction of the cmc in water at 25 °C, of 6.5 and 4.5 times, respectively.



Figure 1. Curves of electrical conductivity (S/cm) versus surfactant concentration (mmol/L) for sodium dodecyl sulfate (SDS) and anilinium dodecyl sulfate (DS-AN)

#### **Kinetics**

Figure 2(a) illustrates conversion (%) versus time (min) profiles for the systems containing different concentrations of DS-AN. Final latexes conversions were in the range from 80 to 90 %. It is observed that the kinetic curves were dependent on surfmer concentration. This behavior is the commonly reported and is related to the dependence of the total particle surface area with respect to the surfactant concentration. These details of emulsion polymerization have been discussed deeply in literature [9]. Thus, at the very beginning of the polymerization, Interval I, the number of polymer particles formed (nucleation period) depends on the surfactant concentration. This way, during the polymerization the monomer was polymerized in a larger number of polymer particles for higher surfactant concentrations; consequently, higher rates of polymerization were observed. Figure 2(b) shows the curves of rate of polymerization (mol/Lmin) versus time (min). As can be seen, the maximum values of the rate of polymerization were dependent on the concentration of surfactant, as mentioned above. These maximum values appeared during the first 15 min; it was also noticeable that the curves followed, at least in certain degree, the behavior suggested for the Smith-Ewart model [10]; i.e., the curves for the polymerizations at 10 and 20 mmol/L of DS-AN presented clearly the three Intervals of emulsion polymerization; however, with 40 mmol/L of DS-AN, Interval II was poorly perceptible. This was due to the high rate of polymerization at this concentration; in fact, as observed in Figure 2(a), the polymerization reached the maximum conversion during the first 20 min. So, the Interval II was very short and Interval III was reached rapidly.



Figure 2. Curves of Conversion (%) versus time (min) (a) and curves of Rate of polymerization (mol/Lmin) versus time (min) (b) for the emulsion polymerizations stabilized with DS-AN at 10, 20 or 40 mmol/L

#### Shell synthesis

The second stage of the composite synthesis was performed via oxidative polymerization. With this technique the PANI shells were deposited. In this stage, only the latex with the highest content of surfmer was considered (40 mmol/L). Thus, more DS-AN was added as the monomers of PAni. The polymerizations were stable after 48 h and precipitation was not observed. In this stage, there were several changes in the appearance of the systems. At the very beginning of oxidative polymerization the latex was white; whereas that after ~10 min and ~15 min the latex turned pale yellow (leucoemeraldine) and dark blue (pernigraniline), respectively. Finally, after ~30 min the latexes acquired a dark green color (emeraldine salt), which varied very little thereafter. The observed changes in color were evidences of the different oxidative states of PAni. Figure 3 shows micrographs of the core-shell latexes; in the pictures it is clear that there was no formation of either clots or separated phase of PAni. This indicated that most of the PAni polymerized on the polymer particles surface. It is also important to emphasize that core-shell particles surface was rougher than in the pristine latex, showing the presence of the PAni shell. Besides, the particle diameters were in the order of 67 nm; that is, ~20% larger than the pristine latex (56 nm), which perfectly evidenced shell formation.

#### Conductivity

Conductivity measurements of the core-shell composites containing ~20 wt% of PAni were performed. For this, probes in the form of disk were prepared. The 4 pin probe procedure indicated conductivities ( $\sigma$ ) of 10-4 and 10-3 S/cm for the composites; that is, in the range of semiconducting materials.



Figure 3. Micrographs of (a) latex particles of polystyrene (40 mmol/L) and (b) core-shell composite after oxidative polymerization.

### Conclusions

The activity of anilinium dodecyl sulfate as surfmer was clearly evidenced in this work. Organic counterion manifested its presence by the reduction of the cmc with respect to the conventional salts. anilinium dodecyl sulfate was successfully employed as stabilizer in true emulsion polymerizations of styrene. Results suggested that this surfactant followed the mechanism of diffusion involved in emulsion polymerization. The function of anilinium dodecyl sulfate as surfmer was truly versatile, thus, the next features can be highlighted: (a) anilinium dodecyl sulfate allowed the synthesis the PAni shell via oxidative polymerization with no addition of acid and (b) no residuals of surfactant are needed to be eliminated, since each molecule of surfactant present in the system is potentially a monomer for PAni synthesis.

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# SEMICONDUCTING CORE/SHELL NANOPARTICLES OF POLYPYRROLE/METHYL METHACRYLATE BY MICROEMULSION POLYMERIZATION

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### Abstract

In this work, we are presenting the synthesis of core/shell nanoparticles of PPy/polymethyl methacrylate (PMMA), using the methodology developed by our group reported in reference [4] in order to obtain the PPy core and adding methyl methacrylate by a semicontinuous process to form the shell. The effect of MMA addition rate on the thickness of shell was studied.

# Introduction

To date, the fabrication of transparent conductive thin films has been largely dependent upon inorganic and metallic materials, whereas little attention has been paid to the use of nanoparticles of conductive polymers dispersed into a matrix. Recently, conductive polymers with conjugated double bounds have received great attention to be used in conductive thin films. Particularly, interest in PPy has been growing due to its good environmental stability, facile synthesis and high electrical conductivity [1]. The chemical polymerization of pyrrole is particularly important because this route is more feasible for the large scale production of PPy [2].

The production of nanoparticles of polypyrrole can be achieved taking advantage of microemulsion systems. Microemulsions are thermodynamically stable and are formed spontaneously by mixing an organic and an aqueous phase in the presence of a surfactant in the proper amounts. Yan et al. [2] prepared conductive PPy nanoparticles by microemulsion polymerization using ferric chloride (FeCl<sub>3</sub>) as oxidizing agent, sodium dodecyl benzenesulfonic acid (SDBA) and n-butyl alcohol as the surfactant and co-surfactant, respectively. The Dp of the resulting latexes were between 30 and 50 nm; nevertheless, the SDBA concentration used in their recipes was near 15 wt.% and the final PPy content was only around 0.02 wt.%, which is very low for practical applications.

To date, the report by Liu et al. [3] is the only one addressing the control of the structure of the PPy chain through microemulsion polymerization. They studied the influence of short chain alcohols on the properties of PPy nanoparticles synthesized using SDS as surfactant, and ammonium peroxydisulfate as oxidant and reported that particles with average diameter around 30 nm were obtained when using in the recipe 2 wt.% of SDS, a molar ratio of oxidizing agent to pyrrole near to 1.0 and 0.5 wt.% of pyrrole and that the conjugation and order of PPy chains were improved by the presence of alcohols. However, the form in which the alcohols act controlling the double bounds conjugation has not been fully understood yet.

In this work, the synthesis of PPy nanoparticles with narrow size distribution by o/w microemulsions stabilized with low concentration of SDS as surfactant and ethanol as co-surfactant and using low concentrations of the oxidizing agent (KPS) is reported. The effect of alcohol concentration on the polymer structure and particle size is also reported.

# **Experimental**

SDS was purchased from Hycel (Guadalajara, Mex.) ( $\geq$  98%); all the other reactants were purchased from Aldrich (St. Louis, MO) (≥99%) and were used as received. Bi-distilled grade water and argon of ultrahigh purity from Infra<sup>TM</sup> were used. The one-phase o/w microemulsion regions were determined visually by titrating aqueous micellar solutions of known concentrations of SDS with the pyrrole monomer. The recipes are given in Table 1.

# **Polypyrrole core obtention**

The polymerizations were carried out at 20 °C in a four-neck 1 L glass – jacketed reactor equipped with mechanic stirring and reflux condenser. The KPS was dissolved in 5 g of water and the surfactant, the ethanol and the rest of the water were charged to the reactor; afterwards, the system was purged with argon for one hour to remove oxygen. Then, the mixture was brought to the reaction temperature and the monomer was added to the reactor. After 10 more minutes, the KPS aqueous solution was added in one shot to initiate the polymerization. The reactions were allowed to proceed for three hours to obtain a dark reaction mixture.

# **Shell formation**

The latex of PPy obtained from Reaction Et-02 was used as core to form core/shell nanoparticles. At the end of polymerization (first step), monomer of methyl methacrylate was added to the reactor continuously to the reactor using a gas-tight syringe (Hamilton GASTIGHT<sup>®</sup>) adapted to a calibrated addition pump (Kd-Scientific<sup>®</sup>). After the semi-continuous addition period the reactions were allowed to continue for 30 minutes.

The resulting latexes were analyzed using UV/Vis spectroscopy (Genesys 10, Thermo-Spectronic). Polymer samples were purified evaporating the water and residual monomer under reduced pressure. Then methanol was added to dissolve the surfactant and oxidizing agent and the polymer was separated by decantation and dried at 40 °C for 24 hours. For the morphology and particle size determination and distribution, a 1:1000 water dilution of the latex was used. A drop of the diluted latex was poured on a copper grid coated with Formvar<sup>TM</sup> resin and carbon film and then, it was allowed to dry overnight at room temperature. The samples were analyzed by Scanning Transmission Electron Microscopy (Philips scanning electron microscope model XL30 FEG).

Table T Recipes used in the reactions.						
	Reaction <sup>a</sup>	Ethanol	SDS	Water	KPS	Ру
	Et-01	0.000	10.5	337.50	0.06	1.75
	Et-02	3.500	10.5	334.37	0.06	1.75
	Et-03	6.125	10.5	331.56	0.06	1.75
	Et-04	8.750	10.5	328.94	0.06	1.75

<sup>a</sup> All the amounts are in grams

# **Results and Discussions**

Table 1 Desires used in the resetions

The initially translucent microemulsions turned light green when polymerization started and became black at the end of the reaction. The final latexes contained 0.5 wt.% of PPy and no phase separation was observed after three months of storage. Figure 1 shows that in all cases spherical nanoparticles were obtained. The average final particle sizes and the polydispersity index are shown in Table 2. Figure 2 presents the particle size distribution (PSD) obtained counting at least four hundred particles. This Figure and Table 2 show that the presence of the



alcohol increases particle size and that the PSD and PDI can be controlled by the addition of alcohol, the larger the amount of alcohol the smaller the PDI.

Figure 1 Transmission electron micrographs of diluted polypyrrole latex obtained at different alcohol concentrations.

Run	$D_n^{\ a}$	$D_{v}$	$D_w$	$D_z$	PDI
Et-01	19.1	20		25.2	1.2
Et-02	38.7	40.9	45.2	51.8	1.2
Et-03	45.3	47.7	52.6	61.0	1.16
Et-04	44.3	45.8	48.5	52.4	1.09

**Table 2**  $D_n$ ,  $D_v$ ,  $D_w$ ,  $D_z$  and PDI obtained by TEM of final latexes for different alcohol concentrations.

<sup>a</sup> Diameters are given in nm

Polymer chain structure

In Figure 3, the UV/Vis spectra of the polypyrrole latexes obtained are shown. It can be seen two absorption bands, one between 420 and 480 nm and the other around 900 nm, these bands are present in oxidized polypyrrole. These two signals have been attributed to transitions of the valence band to polaron and bipolaron/polaron states. The ratio of the two absorbance maxima mirrors the doping level of the polymer which is dependent on the degree of oxidation and the

length of conjugation. This ratio decreases if the polymer is reduced or over oxidized. From Figure 3, the peak maximum for Et-01 (alcohol free) is obtained at 440 nm, while by the addition of alcohol (Et-02) there is a shift of the maximum peak to 450 nm, and for the Et-03 and Et-04 the maximum is at 458 nm. However, the maximum peak corresponding to the bipolaron state decreases when alcohol concentration increases (from 970 nm for Et-01 to 885 nm for Et-04). Usually, the bipolaron state is observed when some dopant agent is present in the conducting polymer chain, in our case; the bipolaron state is due to the presence of the surfactant (SDS), which has been reported in other works acting as a dopant agent by associating with the positive form of PPy.



Figure 2 Particle size distributions of the latexes obtained in the different runs.

Typically, most chemical oxidation reactions to obtain conducting polymers are carried out by addition polymerization reactions and its mechanism is different from that of electrochemical polymerizations. Scheme 1 describes the chemical oxidation mechanism of pyrrole. The initiation step implies the pyrrole monomer oxidation and the formation of radical-cations of  $C_4NH_5^+$  and radical coupling between two radical-cations giving a dimer with deprotonation leading to a bi-pyrrole. The bi-pyrrole is reoxidized and couples with other radical-cation. This process is repeated through the propagation step. Termination occurs by a nucleophilic attack of water molecules or impurities to the polymerization by chemical oxidation. In the case of monomer-monomer coupling, protons of  $\alpha$  positions are eliminated easier than those in the  $\beta$  position. The  $\alpha, \alpha$  coupling makes a major contribution to the coupling reaction and leads to a linear PPy. This  $\alpha, \alpha$  coupling of alternating pyrrole units provides a high degree of  $\pi$ -conjugation (interactions  $\pi-\pi*$ ). Conversely,  $\alpha - \beta$  coupling occurs to the same degree and forms a crosslinked PPy chain, breaking the linearity and planarity of PPy chains.

As reported by Liu et al. [3], the presence of the alkyl unit of alcohols adjusts the PPy structure by  $\alpha, \alpha$  coupling. These changes in the molecular structure lead to the improvement in the electrical conductivity. It is well known that short-chain alcohols can act as effective cosurfactants to lower the interfacial energy further and optimize the structure of PPy chains during interfacial polymerization. The interaction between the hydroxyl groups of the alcohols and the nitrogen atom of pyrrole plays the major role in determining the molecular structure in PPy nanoparticles allowing  $\alpha, \alpha$  coupling events. The amounts of alcohol used in our experiments increased the conductivity of PPy chains by increasing the  $\pi$ -conjugation length, the particle size was increased too, but it was smaller than 50 nm.



Figure 3 UV/Vis spectra of final PPy nanolatexes obtained at different alcohol concentrations

Scheme 1 Chemical oxidation polymerization of pyrrole.

The results corresponding to core/shell morphology will be presented at the congress.

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# INCORPORATION OF MESOPOROUS SILICA-BASED METAL PRECURSORS IN NYLON 6

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# Abstract

The introduction of electrically conductive fillers into polymeric matrices is a promising approach to fabricate electrically conductive polymeric materials. In this study, metal-impregnated inorganic mesoporous silica (MCM41) was used in order to prepare hybrid nylon 6 polymeric products. The metal precursors were obtained by incipient impregnation using aqueous solution of metal nitrates  $[(AgNO_3, Cu(NO_3)_2 \cdot 3H_2O)[1]$ . It was first assumed that mesoporous silica, having a high surface area, would allow high dispersion of metal nanoparticles onto the mesoporous structure. The precursor powders were characterized by X-ray diffraction, physical adsorption, transmission electron microscopy and conductivity tests. The results showed that the incorporation of metals in mesoporous silica did not change its crystalline structure. Contrary to expected the conductivity tests of these powders gave place to only slight changes suggesting the need of optimization. Nevertheless, the resultant powders were used to obtain hybrid nylon 6 products, the best reaction conditions having been determined on the basis of those typically used in the nylon 6 synthesis. [2]. Several experimental techniques were also used in order to characterize the nylon 6 nanocomposites. Thermal analyses after isothermal crystallization indicated multiple fusion, rather similar to the homopolymer. The hybrid products however showed an increase in Young's modulus of 33%. The polymer nanocomposite fibers generated also a small increase in conductivity.

# Introduction

The field of nanostructured materials has been the subject of extensive research in recent years, because the size of the nanostructures plays an important role in their optical properties, electrical and magnetic, hence the importance of developing methodologies that allow synthesis have control over the size of them and so have materials with desired properties.

Mesoporous materials represent an opportunity to obtain nanostructures of controlled size; the discovery was made by researchers at the Mobil Oil Corporation [3]. The structure of the silica MCM-41, consisting of one-dimensional cylindrical pores, which are arranged in hexagonal arrays, with high surface area (1000 m<sup>2</sup>/g) and large pore volume, uniform pore size (2-50 nm), and high thermal and chemical stability. It was first assumed that mesoporous silica, having a high surface area, would allow high dispersion of metal nanoparticles onto the mesoporous structure. Metal nanoparticles and nanowires find immense applications in the field of electronic technology [4] as well as catalysis [5] due to their unique electrical, magnetic, optical and other properties arising from the prospective applicability of their quantum size effect.

En relation to the polymer matrix, Nylon 6 is a semicrystalline thermoplastic polymer, high-level industrial application. The nature of Nylon 6 favors the polymer chains are flexible enough to crystallize, which can naturally crystallize in monoclinic structures  $\alpha$  and  $\gamma$ -pseudohexagonal. The presence of a structure or another is determined by the cooling rate, the crystallization temperature and molecular weight [6]. With the incorporation of metal nanoparticles in mesoporous silica matrix and subsequent hybridization with the Nylon 6, it strives to change in relation to the electrical properties, mechanical properties and antibacterial properties.

# Experimental

## MCM-41 synthesis

To synthesize the MCM-41, CTAB (cetyltrimethylammonium bromide) was dissolves in water and heated slightly (35-40°C) for 30 min to dissolve completely the surfactant. Was add a solution 2 M of NaOH and finally TEOS (tetraethyl orthosilicate) the silicate source. The final composition of the gel was  $SiO_2:Na_2O:CTAB:H_2O:8.4:2.1:1.0:1108.9$ . The resulting mixture was stirred rapidly at room temperature for 2 hrs. and after this time the mixture is heated to 120 °C in a bath of glycerol for 72 hrs. [7]. Samples were then collected by filtration, washed with 50 mL of water, and air-dried.

After the synthesis process, the material is subjected to post-synthesis hydrothermal stabilization [8]. Finally we proceed to the removal of organic material, which is done through the calcination of MCM-41 at 550 °C under nitrogen flow for 2 hrs. followed by a flow of oxygen for 4 hrs.

The metal precursors were obtained by incipient impregnation using aqueous solution of metal nitrates  $[(AgNO_3, Cu(NO_3)_2 \cdot 3H_2O) [1]$ . In the impregnation method, only using the volume of solution required to completely fill the pores of the support. The impregnated material was dried at 100 °C to remove water content. Subsequently, these materials are subjected to calcination; this step aims at total decomposition of the precursor (removal of the organic part). Finally the samples were placed in a tube furnace, and the metal precursors were reduced under a constant H<sub>2</sub> flow. The reduction temperatures for Ag, and Cu precursors were 350, and 540°C, respectively.

### **Polymer synthesis**

The resultant powders were used to obtain hybrid nylon 6, the best reaction conditions having been determined on the basis of those typically used in the nylon 6 synthesis [2].

Hybrid synthesis was made in a Parr 4520 batch reactor using  $\epsilon$ -caprolactam and 13 wt % aminocaproic acid as initiator, also incorporated MCM-41 (2 wt %). The temperature is raised gradually to 100 °C and held for 1 hour with stirring, allowing the homogenization of the reactants. The reaction conditions were automatically set in the reactor using nitrogen atmosphere at 21 psia of pressure. The hybrid products were water washed at 80 °C for 30 min, and then vacuum dried at 80 °C for 48 hrs.

# **Fiber extrusion**

In polymer extrusion, raw materials are placed in a hopper and fed into the barrel. The barrel contains a screw that mixes the particles and transported to the heating chamber where the polymer melts, the mixture finally passes through a die extrusion. The equipment used is a laboratory extruder brand mini Dynisco model LME-120 operated at a temperature of 260 °C in the mixing chamber and 250 °C on the die, with a residence time of 35 seconds and a top speed of 40 rpm.

# **Experimental techniques**

Within the experimental techniques used in the characterization of mesoporous materials and hybrid products are: X-ray diffraction wide-angle (WAXD), this technique was used in the structural characterization of mesoporous materials, incorporation of metals in MCM-41 and the study of crystallization isothermal hybrid products. Nitrogen physisorption, which was used in the determination of surface area, pore size and pore volume distribution function of the radius of the mesoporous material. Spectroscopy Fourier Transform Infrared (FTIR) in the hybrid products

allowed us to determine the molecular weight based on the extent of the relationship intensity between the stretching vibration of carbonyl group (C=O) 1630 cm<sup>-1</sup>, present in both the monomer and the polymer, and the scissors vibration of the amide group (C-N-H) present only in the polymer chain [2]. Differential Scanning Calorimetry (DSC) which was used to study the thermal properties of hybrid polymers (isothermal crystallization followed by melting). Finally, mechanical tests were carried out effort against deformation and conductivity test.

# **Results and Discussion**

Mesoporous materials develop an orderly three-dimensional structure generated by diffraction peaks at certain angles, the silica MCM-41 shows three intense peaks associated with the diffraction orders (100), (110) and (200). Figure 1 shows all the diffraction peaks for MCM-41 silica, confirming the achievement of this structure.



for the sample of MCM-41.

Figure 2. Diffraction pattern of X-rays to MCM-41 silica impregnated with metal particles.

Figure 2 shows the diffraction pattern of mesoporous silica impregnated with metal particles, are observed diffraction peaks corresponding to each of the metals. It can be seen, the presence of diffraction planes (110) and (200) for the MCM-41, indicating that the mesoporous silica is stable to the process of incorporation of nanoparticles of copper and silver, retaining the hexagonal structure.

Table 1. Pore diameter and conductivity of MCM-41 and impregnated samples

Sample	Pore diameter (nm)	Conductivity (S/m)
MCM-41	3.5	$6.5*10^{-8}$
MCM-41-Ag	3.8	7.2*10 <sup>-7</sup>
MCM-41-Cu	3.6	5.5*10 <sup>-7</sup>

According to the results of physisorption, the pore diameter increases slightly, indicating that the metal is deposited on the walls of the silica. Also according to the conductivity test, this is increased by an order of magnitude due the incorporate the metal particles.

Semicrystalline polymers are amorphous part where the molecules are random, but if subjected to a deformation, it is possible that these molecules are ordered in the sense of strain. The  $\gamma$ -type crystalline phase pseudohexagonal crystalline structure is observed only in samples oriented crystal that generates two reflections, one at (002) and another at (001) as shown in Figure 3,

although the modified mesoporous silica incorporating some these reflections. Based on Figure 4, we determined the molecular weights of nanocomposites, according to the methodology described above.



**Figure 3**. Pattern of X-ray diffraction for fibers of Nylon 6-MCM-41.

Figure 4. IR spectra of Nylon 6 homopolymer commercial, Nylon 6 and Nylon nanocomposites.

According to Figure 4 shows a high concordance between patterns of FTIR to Nylon 6 of reference and samples synthesized. The average molecular weight of polymer products does not change significantly. It also generates an increase in the modulus of elasticity. The conductivity does not show a significant change.

Sample	Mn (g-g/mol)	Young's modulus (cN/tex)	Conductivity (S/m)
Nylon 6	15964	125.4	$2.19*10^{-14}$
Nylon 6-MCM	15830	163.8	$2.21 \times 10^{-14}$
Nylon 6-MCM-Ag	15820	166.9	$2.21 10^{-14}$
Nylon 6-MCM-Cu	15825	172.3	$2.40^{10}$ 2.32*10 <sup>-14</sup>

Table 2. Molecular weight obtained by IR, Young's modulus and conductivity of fibers.

# Conclusions

We performed the synthesis of MCM-41 silica with high surface area and pore size in the range of mesopores. The process of incorporation of metal nanoparticles in mesoporous silica retains the hexagonal structure, and increases by an order of magnitude the conductivity of the same.

Samples of Nylon 6 and MCM-41 (Ag, Cu) obtained by extrusion of the polymer produced oriented fibers, which showed the  $\gamma$ -pseudohexagonal crystalline phase characteristic of these materials. It also confirmed the presence of the metal species in the fibers obtained. The incorporation of mesoporous silica in the polymer matrix shows a slight decrease in molecular weight, it also generates an increase in the modulus of elasticity due of 33% to the reinforcing effect of silica. The conductivity does not show a significant change

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# ION-EXCHANGEABLE ZEOLITES AS SUPPORT IN THE SYNTHESIS OF SILVER NANOPARTICLES: ANTIBACTERIAL EFFECT IN POLYPROPYLENE NANOCOMPOSITES

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# Abstract

In the present work, we consider the use of a ZeoliteW with general formula  $K_{10.32}(Si_{21.7}Al_{10.3}O_{64})$ . H<sub>2</sub>O as efficient tool to exchange K<sup>+</sup> by Ag<sup>+</sup> in aqueous solution and finally the obtention of silver nanoparticles and clusters of them by chemical reduction (decorated Zeolites with AgNP's into the cavities and surfaces). After the obtention of ZeoliteW@AgNP, the production of nanocomposites by melt compounding was carried out using a Micro-Extruder (corotatory twin screw) and polypropylene as polymeric matrix. Finally different polypropylene surfaces (PP-ZAgNP) were obtained by injection moulding and antibacterial activity against E. Coli and S. Aureus was evaluated acoording with japanese standard method JIS-Z2801 (Antimicrobial products-Test for antimicrobial activity and efficacy) [1].

# Introduction

Antimicrobial materials play an important role in the academic and technological fields due to applications in food packaging and medicinal devices. There are many antimicrobial materials with good efficiency based in organic/inorganic hybrids. Recently, many nanocomposite materials based on thermoplastic polymers have been used as support matrix in order to obtain materials with improved antimicrobial effect using silver nanoparticles (AgNP's) [2]. On the other hand, many efforts have been focused towards the incorporation of metal nanoparticles on inorganic porous materials, in this way, the inorganic material have the abbility of act as a carrier of nanoparticles. Zeolites are a kind of aluminosilicates which possess the peculiarity of ionic exchange, specially towards cation substitution [3].

### Experimental Synthesis of Zeolite@AgNP

Procedure of the synthesis of Zeolite decorated with silver nanoparticles (Zeolite@AgNP) is showed in Figure 1, basically an aqueous solution of Zeolite W was inmersed in silver ions under different conditions of stirring and time, finally silver ions were reduced by NaBH<sub>4</sub> aqueous solution



Figure 1. Synthesis of Zeolite@AgNP by chemical reduction of silver ions.

# Melt compounding: Extrusion and Injection Moulding

In order to obtain nanocomposites based polypropylene (PP), melt compounding by extrusion was carried out using a Micro-Extruder (corotatory twin screw) with five temperature zones (the Figure 2 shows the diagram). The nanocomposites obtained were injected for the obtention of samples, which were cut at  $1x1 \text{ cm}^2$  for the bactericidal evaluation.



Figure 2. Obtention of Nanocomposites by extrusion.

# **Bactericidal Evaluation**

Minimum Inhibitory Concentration (MIC) was determined with an aqueous solution of ZeoliteW@AgNP with 0.005M concentration of silver. Bacteriostatic concentration was determined by micro dilutions following the standard M7-A7 Vol 23 No. 2 CLSI (2006) (Methods for Dilution Antimicrobial Susceptibility Test for Bacteria That Grow Aerobically), S. aureus (resistant) and E. coli (ATCC95922) was used in this evaluation. Table 1 shows the results taking into account the MIC obtained.

# **Results and Discussion**

Figure 3 shows the morphology of the pristine ZeoliteW and it can observed that the synthesis of AgNP's was succesfully reached, and their sizes are in nanometer range. The EDAX analysis shows an homogeneous distribution of the AgNP's in the Zeolite matrix.



Figure 3.SEM micrographs of: a) Pristine Zeolite W, b), c) ZeoliteW@AgNP

Figure 4 shows the XRD patterns of pristine ZeoliteW and even when an overlapped of peaks, it is important to note an increased of the peak at 38.2° due to (111) plane of face centered cubic (fcc) structure of silver nanoparticles.



Figure 4.XRD patterns of Pristine Zeolite W and ZeoliteW@AgNP.4.

Results of the bactericidal effect will be discussed in the talk.

#### Conclusions

ZeoliteW results as an excellent candidate for the support of AgNP's thanks to its abbility of ionexchange (mainly due to the presence of  $K^+$  cations). PP-ZAgNPs nanocomposites prepared by extrusion and injection moulding were effective against E.Coli and S.Aureus growth.

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# EFFECT OF ZINC OXIDE NANOPARTICLES CONCENTRATION ON THE MECHANICAL PROPERTIES AND UV PROTECTION OF IN SITU SYNTHESIZED ABS BASED NANOCOMPOSITES

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### Abstract

A series of ABS/ZnO nanocomposites with different nanoparticles content were synthesized by mass-mass and masssuspension process. Because nanocomposites obtained through mass-suspension process had a greater impact resistance than those derived from mass-mass processes, they were subjected to twin-screw extrusion. The extrusion led to a dramatic morphological change and increased in impact resistance, higher than 100% in most of the cases. On the other hand, the higher the ZnO content, the higher the UV blocking (>95% for 1 and 3% of ZnO) for both materials, before and after extrusion.

### Introduction

Acrylonitrile-butadiene-styrene copolymer (ABS) is a well-known rubber-toughened thermoplastic that displays several attractive properties, such as impact resistance, solvent resistance, and good processability. Due to these features ABS is used in various industries, mainly automotive and appliances. However, the rubber particles embedded into the poly(styreneco-acrylonitrile) (SAN) matrix have an inconvenient, they absorb UV radiation due to the presence of carbon-carbon double bond in the inner structure, limiting outdoor applications [1]. In order to avoid this drawback, several compounds, generally organic material, known as UV stabilizers have been used. Among the widely UV stabilizers used are: hindered amine light stabilizers (HALS), benzotriazoles and benzophenone derivatives, just to mention some [2]. Recently, the incorporation of nano-zinc oxide (nano-ZnO) into polymer matrices, such as PMMA [3], PET [4], PP [5], PAN [6] and PS [7], has gained importance. This metal oxide possess advantages over commonly used organic UV stabilizers, for example, it does not migrate to the plastic surface, exhibit broad-band UV absorption, good chemical stability under high temperature and UV radiation, and antibacterial properties, among others. Furthermore, polymer/ZnO nanocomposites showed improved thermal stability [3], elongation to fracture [8], and excellent resistance to photo-degradation [4-7]. Therefore, nano-ZnO is a candidate with great potential to be used as UV protective additive in ABS resins. However, good dispersion of nanoparticles is required in order to prevent a decrease in impact resistance of ABS, in situ polymerization technique was used in order to obtain a well-dispersed nanocomposites as was previous demonstrated [3-4].

## Experimental

### Synthesis of ABS and ABS/ZnO nanocomposites

ABS and ABS nanocomposites were prepared as follows: in a 1 gallon capacity stainless steel reactor, with an anchor-turbine stirrer: (i) 6 wt% of polybutadiene (PB, Diene 40 by Firestone) with respect to monomers was dissolved in a mixture of styrene/acrylonitrile (77.4/22.6 wt%) at a stirring rate of 30 rpm and at room temperature for 15h, (ii) 0.025 wt% of benzoyl peroxide (BPO), 0.2 wt% of tert-dodecyl mercaptane (TDM) and in the case of nanocomposites 0.05 to 3wt% of nano-ZnO were added to the reaction mixture, the stirring rate and temperature were

increased to 60 rpm and 85°C, respectively, and the stage of stirred mass-polymerization took place until the monomer conversion was close to 13-18%, (iii) a certain amount of the reaction mixture was collected in test tubes, which were introduced into an unstirred reactor containing distilled water, the reactor was closed, purged and pressurized at 120 psi, the temperature was increased at 125°C for 5h, then at 150°C for 15h, (iv) 0.1wt% of tert-butyl perbenzoate (TBPB) and a suspension medium were added to the remaining mixture in the reactor. During this stage stirring rate was increased to 700 rpm at 125°C for 2h and afterward to 150°C for 5h. The suspension medium was constituted by distilled water (2 L), polyvinyl alcohol (3.5 g), sodium chloride (3.5 g), and nonyl phenol (0.9 g).

Regarding to extrusion of materials, it was performed in a co-rotating twin-screw extruder with a screw diameter (D) of 24 mm and L/D ratio of 40. The Figure 1 shows the extruder configuration where the temperature of each zone was: 2-4 at 200°C, 5-7 at 220°C, 8-die at 240°C, while the screw rotating rate was 40 rpm.



Figure 1. Extruder configuration used for the ABS's obtained through mass-suspension technique

# Molecular, morphological, mechanical and spectroscopic characterization of ABS and nanocomposites

The grafting degree (GD), defined as the ratio between the mass of grafted SAN branches (without the initial PB) and the original PB fraction in the recipe, was calculated by the equation:

$$GD = \frac{Gel\% - PB\%}{PB\%} X \, 100$$
 Eq. 1

where the gel% and PB% are the weight fractions of tetrahydrofurane insoluble and original PB, respectively. The gel% was isolated from the soluble fraction (SAN matrix) using the centrifugation technique (45 min at 20,000 rpm at -10°C). The soluble fraction was precipitated from methanol, and both fractions were dried to constant weight. Number-average molecular weight ( $M_n$ ) of the SAN matrix was determined by size exclusion chromatography (SEC). With respect to morphological parameters, number-average particle diameter ( $D_n$ ), and volume fraction of the rubber phase ( $\Phi$ ) were estimated from TEM micrographs. Notched Izod impact resistance tests were carried out according to ASTM 256 at 25°C on compression-molded specimens. With respect to UV protection, the transmission spectra of ABS films (thickness of 250 ± 5 µm) were obtained in a wavelength range from 200 to 500 nm.

### **Results and Discussion**

Figure 2 shows the morphology of the ABS and ABS/ZnO nanocomposites, it can be seen that regardless of the polymerization process used (i.e. mass-mass or mass-suspension), the rubber particles have SAN occlusions (salami structure). However, average particle diameter derived of the mass-suspension process is slightly lower than those obtained by mass-mass, which may be due to a greater grafting degree of the material obtained by the former process (see Table 1), that induces a lower interfacial tension [9].

With respect to impact resistance and comparing the methods used for the synthesis of ABS and ABS/ZnO nanocomposites (see Figure 3), the materials obtained by mass-suspension process showed a better mechanical performance (except blank, see Table 1), which can be attributed to higher GD, molecular weight and probably to a better dispersion of nanoparticles [9-10], although in the corresponding micrographs of materials synthesized by suspension agglomerates are still observed (Figure 2f-j), even though they are smaller in comparison with those observed in materials obtained from the mass-mass process.

On the other hand, when the ABS's produced through mass-suspension process are analyzed and compared to the blank ABS, it can be observed that impact resistance shows a little variation (~98 J/m) despite the presence of agglomerates at high nanoparticles content, furthermore with a 0.05 wt% of nano-ZnO impact resistance increased by 11%. The reason of improvement in impact resistance for this nano-ZnO content is a combined effect of molecular weight, GD and dispersion of metal oxide and a probable effect of  $\Phi$  was discarded because for all the materials was 0.342±0.01 [11].



**Figure 2**. Micrographs of ABS and ABS/ZnO nanocomposites obtained by mass-mass process (a-e), mass-suspension process (f-j) and extruded materials (k-o) with 0, 0.05, 0.166, 1 and 3 wt% of nano-ZnO (content increases from left to right).

Table 1.	. Molecular and	l morphological	parameters of AB	BS and ABS/ZnC	) nanocomposites
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		r o r								
Nano-ZnO	M <sub>n</sub>				GD			$D_n$		
(wt%)	(kg/mol)				(%)			(µm)		
	М	S	Е	М	S	Е	М	S	Е	
0	53.9	77.9	66.9	1216	1007	646	1.50	1.25	ND	
0.05	72.7	96.8	72.5	398	599	242	1.64	1.49	ND	
0.166	50.9	86.5	64.8	174	382	362	1.69	1.65	ND	
1	52.6	76.0	72.4	140	210	490	1.82	1.56	ND	
3	54.5	80.0	68.7	195	247	614	1.74	1.55	ND	

M = Materials obtained by mass-mass process, S = materials obtained by mass-suspension process, E = mass-suspension extruded materials,  $M_n =$  number-average molecular weight, GD = grafting degree and  $D_n =$  number-average particle diameter.

On the other hand, the extrusion of ABS's synthesized by mass-suspension process caused a dramatic morphological change, since rubber particles changed from a salami type morphology to homogeneous rubber particles (practically without occlusions). Moreover, despite the loss of integrity of the elastomeric particles (and consequently a drop of all morphological parameters), surprisingly the impact resistance doubled. This increase in impact performance is probably due to morphological similarity between extruded materials and ABS produced by emulsion polymerization process, which posses a higher impact resistance [12].



**Figure 3.** Izod impact resistance of ABS and ABS/ZnO nanocomposites as a function of nano-ZnO content  $(\Box)$  mass-mass process, ( $\blacktriangle$ ) mass-suspension process and ( $\bullet$ ) mass-suspension extruded materials

Concerning to the ability of synthesized materials by mass-suspension polymerization to block UV radiation, Figure 4a shows the UV transmittance spectra. It can be clearly observed that ABS is able to absorb UV radiation, which is inherent to its chemical composition. However, ABS/ZnO nanocomposites showed a continuous decrease of UV rays transmission with increasing metal oxide content, except with 3 wt%. This can be explained in terms of ZnO nanoparticles agglomeration [4]. Once these materials were extruded, the UV spectra followed an expected pattern increasing UV blocking with nano-ZnO concentration (Fig. 4b) [3, 5-7]. In the case of the blank extruded ABS, the decrease in transmittance (apparent increase in UV blocking) can be a consequence of the destruction of rubber particles, therefore, an increase in surface area prone the UV light absorption.



**Figure 4**. UV spectra of ABS and ABS/ZnO nanocomposites obtained by mass-suspension process (a) before extrusion and (b) after extrusion. Content of ZnO: ( $\circ$ ) 0, ( $\bullet$ ) 0.05, ( $\Delta$ ) 0.166, ( $\blacktriangle$ ) 1 and ( $\Box$ ) 3wt%.

### Conclusions

ABS and ABS/ZnO nanocomposites were successfully synthesized by two processes (mass-mass and mass-suspension). The material obtained by mass-suspension process showed higher impact resistance probably due to combined effect of nanoparticles dispersion, morphological and molecular parameters. The extrusion of these materials caused a loss of integrity of elastomeric particles, however, the impact resistance doubled, which can be explained in terms of morphological similarity with commercial emulsion ABS. Finally, the UV blocking is not significantly affected by the extrusion process, since the higher ZnO content, the higher UV protection, yielding >95% for 1 and 3wt% of ZnO.

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# CRYSTALLIZATION AND MELTING BEHAVIOR OF NANOCOMPOSITES OF POLY(L-LACTIC ACID) AND SURFACE-GRAFTED MESOPOROUS SILICAS WITH L-LACTIC ACID OLIGOMER

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### Abstract

Biodegradable poly (L-lactic acid)/mesoporous silica nanocomposites were solution prepared. A surface modification method, using grafting of L-lactic acid oligomer onto surface silanol groups of mesoporous SBA-15 silica, has been developed in order to introduce the appropriate interfacial interactions between the surface of the inorganic nanoparticles and the organic matrix. The surface-grafting reaction was confirmed by IR analysis and the results indicated that L-lactic acid oligomer could be easily grafted onto the mesoporous silica surface, without using silane coupling agents, or catalysts, which are usually toxic [1]. The results of small-angle X-ray scattering (SAXS) and X-ray diffraction (WAXD) were used to determine the effect of the oligomer on the crystal structure of grafted mesoporous silicas and also of the nanocomposites. Neat PLLA had a lower degree of crystallinity than the rest of composites. Grafted SBA-15 nanoparticles in the PLLA matrix greatly improved the tensile strength and the thermal stability of this nanocomposite. Young's modulus of the nanocomposites containing 10 wt/wt % of grafted SBA-15 displayed a double value regarding neat PLLA. DSC analysis indicated that grafted SBA-15 acted as nucleating agent, and, as the silica content increased, the crystallization and melting temperatures also increased. The hydrolytic degradation of PLLA was enhanced after nanocompounding because the amorphous phase was easier to degrade compared with that of the crystalline phase [2]. This last property was considered important for practical applications of these nanocomposites as biomaterials [3].

### Introduction

Poly (L-lactic acid) (PLLA) is a biodegradable thermoplastic polymer which is widely used in biomedical applications because it is biocompatible, producible from renewable sources, and non toxic for the human body [4]. However, the relatively poor mechanical properties and slow crystallization and degradation rates have limited practical applications of this polymer. To overcome this situation, the preparation of nanocomposites with inorganic species is considered a suitable and convenient option [5]. This is in spite that in some cases these materials can be harmful to cells or more toxic than other nanoparticles [6]. Mesoporous silicas are materials that have ordered arrangements of channels and cavities of different geometry with siloxane walls. For example, SBA-15 exhibits 2D hexagonal structure with micropores interconnecting adjacent mesopores [7]. Recent in-vitro studies have shown a bioactive behavior of SBA-15, compared with other mesoporous materials. SBA-15 has also been reported suitable for medical applications [8, 9]. Being the purpose to improve the interactions and adhesion between the inorganic phase and the PLLA matrix, several methods have been developed. Some of them are surface coatings, coupling agents, and the use of other additives. In this study we have prepared mesoporous materials chemically grafted with oligomers of L-lactic acid (LLA) via in situ direct melt polycondensation of LLA without using catalysts [10]. We also have compared the results with non grafted mesoporous silicas. The main purpose was to study the effect of grafting on the crystal structure, together with thermal and mechanical properties and the hydrolytic degradation of PLLA.

### Experimental

The Poly (L-lactic acid), with molecular weight 10,000 g/mol, was purchased from Polysciences Inc. The L-lactic acid (85 wt % aqueous solution) was purchased from Sigma Aldrich.

## Mesoporous silica synthesis

SBA-15 silicas were synthesized as reported by Zhao et al. [11] using a 4.0 g sample of Pluronic P123 triblock copolymer (Sigma-Aldrich) as template. The triblock copolymer was dissolved in water and 120 g of 2 M HCl solution. Then, 8.5 g. of TEOS (Fluka) were added as silica source, and then kept at 308 °K for 24 h with stirring, and at 373 °K for 24 h without stirring. The solid product was filtered, washed with water and subject to a hydrothermal treatment at 373 °K under stirring. The product was filtered and dried in an oven at 363 °K overnight and subsequently calcinated in air for 3 h at 523 K and then 4h at 823 K.

## Grafing of L-lactic acid oligomer onto the surface of mesoporous silicas

The L-lactic acid oligomer was grafted onto the surface of mesoporous silicas through a polycondensation reaction of L-lactic acid without catalysts. The mesoporous silica was incorporated (2.5 wt/wt %) into the L-lactic acid solution. Then, the mixture was sonicated to make a uniformly dispersed suspension. The mixture was dehydrated at 423 °K, first at atmospheric pressure for 2h, then at a reduced pressure of 100 torr for 2h, and finally under pressure of 30 torr for another 4h. The reaction mixture was finally cooled down to room temperature. The L-lactic acid oligomer grafted mesoporous silicas (SBA-15-g-OLLA) were separated by centrifugation and washed with chloroform to completely remove the free L-lactic acid. The separated precipitated was dried in an oven at 343 °K in order to remove the residual chloroform.

## **Preparation of PLLA/SBA-15 nanocomposites**

PLLA/SBA-15 nanocomposites were prepared via solution blending using chloroform as a solvent. The appropiate amount of grafted or non-grafted SBA-15 (5, 10 and 15 wt/wt %) was dispersed into chloroform with sonication. PLLA samples were diluted in chloroform and stirred at 343 °K for 1 h to completely dissolve preparations. The PLLA solution was added to the silica suspension and sonication continued with stirring. Last, The PLLA/Silica solution was poured into a dish in order to evaporate the solvent at room temperature and further drying at 343 °K.

### **Materials Characterization**

Nitrogen adsorption-desorption isotherms were obtained in a Micromeritics ASAP2020 gas adsorption analyzer. Fourier transform infrared spectrometry (FTIR, Bruker Vector 22) was used in attenuated total reflectance (ATR) mode to characterize neat PLLA, SBA-15, and SBA-15-g-OLLA. The differential scanning calorimetry (DSC) traces were obtained in a Perkin Elmer DSC-7 calorimeter. After the corresponding crystallization time, samples were linearly heated at 10 °C/min until the equilibrium melting temperature (473 °K). The wide angle X-ray diffraction (WAXD) patterns were obtained in a diffraction equipment (Siemens D-500). WAXD was used to identify crystalline structures. Small Angle X-ray scattering (SAXS) experiments were performed in a NanoStar Bruker AXS instrument, using an accelerating voltage of 40 kV and a current intensity of 35 mA. Cu K $\alpha$  X-ray, wavelength  $\lambda = 1.5418$  Å, was used as the X-ray source. The tensile tests were performed in an Instron 365 machine at a crosshead speed of 10 mm/min. All the composite films were cut into specimens with constant dimensions (28 X 9 X 0.25 mm). The hydrolitic degradation of neat PLLA and its nancomposites was carried out in a phosphate solution (pH = 7.0) at 37 °C. The degradation was determined by the variation of weight loss as a function of time.

### **Results and Discussion**

Nitrogen adsorption-desorption isotherms of SBA-15 and SBA-15-g-OLLA are shown in Figs. 1A and 1B. Both samples exhibited type IV isotherms, characteristic of mesoporous materials

with microporous contributions. The comparison of SBA-15-g-OLLA (SBET =  $33.47 \text{ m}^2/\text{g}$ ) with the SBA-15 (SBET =  $591.85 \text{ m}^2/\text{g}$ ) shows a marked adsorption decrease. The results suggest that mainly the original mesoporous were filled by the oligomer molecules.



Fig.1. Nitrogen adsorption-desorption isotherms: (A) SBA-15; (B) SBA-15-g-OLLA

X-ray scattering patterns of SBA-5 and SBA-15-g-OLLA are shown in Fig. 2(A). There are three resolved peaks in SBA-15(B) which can be indexed, assuming diffraction mode, as (100), (110) and (200) reflections of a two-dimensional hexagonal mesostructure. SBA-15-g-OLLA shows the same pattern, although the peaks intensity is attenuated because the amorphous L-lactic oligomer is grafted onto the surface of the mesoporous silicas. The SBA-15 images show three well defined rings, and in the SBA-15-g-OLLA this pattern is attenuated.



Fig.2. (A) SXRD patterns of the SBA-15 and SBA-15-g-OLLA; (B) SAXS patterns of the SBA-15 and SBA-15-g-OLLA

FTIR analyses quantitatively validated the grafting reaction. Fig. 3 illustrates the FTIR spectra of neat SBA-15 particles, neat L-lactic acid oligomer and SBA-15-g-OLLA. The results indicate that new absortion bands appear at 1759 cm<sup>-1</sup>, 2946 cm<sup>-1</sup>, and 2999 cm<sup>-1</sup> as a consequence of the grafting reaction. These were assigned to the carbonyl group (C=O), methine and methyl of the L-lactic acid oligomer grafted on the surface of SBA-15 nanoparticles. Non-isothermal melt crystallization and subsequent melting of pure PLLA and its nanocomposites (5, 10, 15 wt% SBA-15-g-OLLA, and 5 wt % SBA-15) were carried out by DSC. Figure 4 shows the DSC traces of samples cooled from the melt at 10 °C/min (first cooling). The results demonstrate that the incorporation of SBA-15 and SBA-15-g-OLLA enhances the non isothermal melt crystallization of the PLLA matrix significantly. This effect is well known as heterogeneous

nucleation. The subsequent melting behavior of pure PLLA and its nancomposites after cooling from the melt at 10  $^{\circ}$ C/min (second heating) is shown in Fig. 3(B), where a complex evolution is observed to additionally motivate a heating exotherm and enhance the main melting curve.



Fig.3. FTIR spectra of pure SBA-15 material, pure OLLA, and SBA-15-g-OLLA



Fig.4. Non isothermal melt crystallization and subsequent melting traces: (A) First Cooling, and (B) Second heating

Figure 5 Shows the Wide and Small Angle X-Ray patterns of pure PLLA and its nanocomposites, which were crystallized at 120 °C for 30 minutes.



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Fig.4. (A) WXRD and (B) SXRD patterns of pure PLLA and its nanocomposites PLLA and its nanocomposites crystallized into the  $\alpha$  form. PLLA showed four main characteristic diffraction peaks corresponding to (010), (200), (203) and (105) reflections. The intensities of diffraction of PLLA, i.e. crystallinity degree, decreased after the nancomposites formation although the same crystalline structure remained. The Small Angle X-Ray pattern of pure PLLA showed only one scattering peak. However, four main characteristic peaks were present in the diffraction pattern of PLLA/SBA-15 nanocomposite. This result indicate the preservation of the nanostructure of SBA-15 when it is incorporated with direct mixing in the PLLA matrix without surface grafting modification. However, when SBA-15-g-OLLA is incorporated in the PLLA matri, the peaks intensity of SBA-15 is attenuated in the nanocomposite pattern because the amorphous L-lactic oligomer is grafted onto the surface of the mesoporous structure.

The mechanical properties, not shown here, indicated that PLLA nancocomposites exhibit a higher tensile strenght and lower ductility. The tensile strenght of PLLA/SBA-15-g-OLLA nancomposites also increase with particle content.

# Conclusions

Grafting of L-lactic acid successfully occured on the surface of SBA-15 nanoparticles. There were chemical linkages formed between the SBA-15 particles and the PLLA, demonstrated through FTIR. There was an important adsorption decrease between SBA-15-g-OLLA (SBET =  $33.47 \text{ m}^2/\text{g}$ ) and SBA-15 (SBET =  $591.85 \text{ m}^2/\text{g}$ ) most probably because oligomer molecules filled up the mesoporous of original SBA-15. SBA-15-g-OLLA had the same scattering pattern as L-lactic acid oligomer, although the peaks intensity was attenuated because the amorphous L-lactic oligomer (OLLA) was grafted on the surface of mesoporous silicas. The incorporation of SBA-15 and SBA-15-g-OLLA was more efficient as nucleating agent than non grafted SBA-15 due to a better and homogeneous dispersion in the PLLA matrix.

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Liquid crystalline elastomers combine the concept of self-organization from liquid crystals with the mechanical properties of elastomers. If the mesogenic molecules are aligned in a uniform direction, yielding liquid crystalline monodomains, the samples show a reversible shape change during the transition from the liquid crystalline to the isotropic phase. Thereby they can yield displacements of up to 400% in length, thus being suitable materials for the production of mechanical actuators.

We have developed synthetic strategies to produce aligned LCE samples with a size in the micro- and in the nanometer region. The main technique applied for this purpose was microfluidics. Thereby, micrometer sized droplets from a nematic liquid crystalline monomer were made and polymerized in a continuous process. When heated to the isotropic phase or exposed to a solvent, the resulting particles showed a reversible shape change. Thereby they transferred from a spherical to a rod-like shape. By processing chiral liquid crystalline materials, cholesteric particles with interesting optical properties were obtained. Using a slightly different microfluidic approach we succeeded in the fabrication of highly aligned fibers from a crosslinked, smectic main-chain polymer. These samples had an infinite length and a diameter between 20 and 50 micrometers. During the phase transition they showed a contraction along the fiber axis, thereby creating strong forces. A second patterning technique applied on liquid crystalline materials was anodized aluminum oxide templating. This allowed the preparation of nanometer-sized wires from polymerized and crosslinked nematic mesogens. The obtained structures showed reversible actuation on a nanometer size scale.

### PHOTO-RESPONSIVE STABLE POLYMERIC NANOPARTICLES

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Polymeric nanoparticles have attracted significant attention due to their promising applications in the fields of drug transportation and medical imaging [1]. Generally, nanoparticles consist of a hydrophilic outer shell and a hydrophobic inner core. Here we demonstrate the ability to create aqueous suspended stable nanoparticles of the hydrophobic homopolymer,  $poly(\varepsilon$ -caprolactone) end functionalized with coumarin moieties. Using nanoprecipitation nanoparticles of coumarin-end functionalized poly( $\varepsilon$ -caprolactone), *i.e.*, CPCL, were prepared in a continuous manner. The resulting CPCL nanoparticles were spherical in morphology with an ~ 40 nm diameter, possessed a narrow size distribution and excellent stability over 4 months. The nanoparticles were stable above the melting point of PCL. Nanoparticle size could be easily controlled by manipulating the concentration of CPCL in the solution. As coumarins are responsive moieties that undergo photoinduced [2+2] cyclodimerizaton and cleavage [2], the interparticle assembly between the nanoparticles could be reversibly adjusted with photo-irradiation. In addition, we found that the CPCL nanoparticles had good cellular uptake properties. Moreover, CPCL nanoparticles could be imaged within the cell due to the intrinsic fluorescence of coumarin.

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# COLLOIDAL STABILITY OF POLY(LACTIDE-CO-GLYCOLIDE) NANOPARTICLES DURING STORAGE: EFFECTS OF MOLECULAR WEIGHT AND CONCENTRATION OF POLY(VINYL ALCOHOL) AS STABILIZER

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### Abstract

The colloidal stability of the poly(lactide-co-glycolide) (PLGA) nanoparticles using poly(vinyl alcohol) (PVA) as stabilizer at different molecular weight (Mw= 13-23, 31-50 and 85-124 KDa) and different concentration (3, 9 and 15 g/L) during storage was studied. The PLGA was synthesized via ring-opening polymerization (ROP) at 130°C using lactide and glycolide as cyclic dimers, and stannous octoate as catalyst and 1-dodecanol as cocatalyst. The PLGA emulsions were obtained at 25°C using the emulsion-evaporation method. In this stage, the particle size (Dp) and PLGA dispersed content (PDC) were depended of Mw of PVA and their concentration. Conform the Mw and concentration of PVA were increased, the colloidal stability in the emulsion was higher. This behavior also was observed during storage, although only was possible to obtain an emulsion stable all the time (28 days) with the PVA= 85-124 KDa at 15 g/L (according to results in Dp and PDC). This result was supported when analyzed the surface area of the nanoparticles obtained during their elaboration and the evolution of the PDC, where the surface area was around of S= 4,100 cm2/cm3 using a concentration of PVA of 9 g/L, and the colloidal stability of the PLGA nanoparticles was higher with the PVA of Mw= 85-124 KDa during storage.

### Introduction

Recent developments in the biomaterial field have been focused on biodebradable copolymers such as poli(lactide-co-glycolide) (PLGA) [1]. Ring-opening polymerization (ROP) has been preferred to get PLGA using various molar ratio of stannous octanoate (Sn(Oct)2) and 1-dodecanol (ROH), as catalyst and cocatalyst respectively [2]. This copolymer is widely used as the material for the drug carriers (films, nanoparticles) and used in the process of the controlled drug release [3]. A preferred method to elaborate nanoparticles is emulsion-evaporation using PVA as stabilizer [4]. It has been established that the stabilizing properties of PVA are dependent on the degree of hydrolysis, molecular weight and concentration [5]. In this work, we studied the last two factors on the colloidal stability of PLGA nanoparticles during storage (25°C). Previously, the PLGA was synthesized via ROP and then, employed to the elaboration of the nanoparticles via emulsion-evaporation.

### **Experimental**

The synthesis of PLGA via ROP was carried out in a 1L glass reactor considering the indicated in the Table 1. The reaction time was 90 min at 130°C using an agitation of 500 rpm. During the synthesis, a continuous flow of argon was used. The lactide/glycolide (LA/GA) theoretical ratio was 88/12 w/w, while the (LA/GA)/Sn(Oct)2 and ROH/Sn(Oct)2 molar ratios were 2000 and 1, respectively.

Ingredients	
LA, g (moles)	308 (2.1388)
GA, g (moles)	42 (0.3618)
Sn(Oct)2, g (moles)	0.5065 (1.25 x 10-3)
1-dodecanol, g (moles)	0.1075 (1.25 x 10-3)
Toluene anhydrous, g	35

Table 1. Recipe used in the synthesis of PLGA via ROP at 130°C

The PLGA obtained was purified by using three cycles of dissolution-precipitation, as dissolvent was used chloroform and as precipitant methanol. The weight average (Mw) and number average (Mn) molecular weights were performed using an Alliance Waters GPC and refractive index as detector; as solvent was employed chloroform HPLC. The 1H-RMN spectrum was carried out at 25°C on a Bruker NMR (500 MHz) spectrometer using chloroform-d as dissolvent. The glass transition temperature (Tg) of the polymer was obtained by TA Instruments DSC at rates of 10°C/min (from 0 to 200°C) under nitrogen flow. The PLGA synthesized was used to prepare nanoparticles via emulsion-evaporation considering the formulations shown in Table 2.

Table 2. Recipes used in the elaboration of PLGA nanoparticles via emulsion-evaporation

Formulation, n°	1	2	3	4	5	6	7	8	9
Mw of PVA, KDa		13-23			31-50		8	5-124	
[PVA], g/L	3	9	15	3	9	15	3	9	15
Aqueous phase									
PVA, g	0.45	1.35	2.24	0.45	1.35	2.24	0.45	1.35	2.24
Water, g	150								
Organic phase									
PLGA, g	7.9								
Ethyl acetate, g	150								

The preparation of each emulsion was follows. First, was necessary to dissolve the PVA in water (aqueous phase) and PLGA in ethyl acetate (organic phase). After this, both dissolutions were mixtures and then, emulsified at 23,000 rpm during 3 min at 25°C. Finally, the emulsion was collocated in an evaporator in order to eliminate the ethyl acetate and form the PLGA nanoparticles disperses in water stabilized with PVA. The difference between each emulsion was the use of Mw of PVA (13-23, 31-50 and 85-124 KDa) at different concentration (3, 9 and 15 g/L). All the emulsions were stored during 28 days at  $\approx 25^{\circ}$ C. In this time, several latex samples were taking in order to study their colloidal stability by light scattering (particle size in the PLGA particle, Dp) and gravimetric form (PLGA dispersed content, PDC).

### **Results and Discussion**

The 1H-NMR spectrum of PLGA synthesized via ROP showed three signals, one at 1.6 ppm, other at 4.75 ppm and other one at 5.3 ppm, corresponding to the protons of methyl (-CH3), methylene (-CH2) and methine (-CH) groups, respectively [1]. By using the integral values was possible to determine the experimental composition of LA/GA in PLGA as show in the Table 3. In this table also are presented the results obtained by GPC and DSC.

Table 5. Characterization of LOA obtained via Rot at 150 C								
	1H-NMR	GPO		DSC				
LA in PLGA	GA in PLGA	Mw	Mn	Tg				
(w%)	(w%)	(KDa)	(KDa)	(°C)				
91.9	8.1	98.1	40.6	50.3				

Table 3. Characterization of PLGA obtained via ROP at 130°C

In the case of DSC, the thermogram exhibited only one Tg value suggesting that the PLGA was formed preferably at random. Besides, PLGA did not exhibit melting temperature (Tm) indicating that the copolymer was in amorphous form.

According to indicated previously (see Table 2), nine emulsions were prepared with the PLGA synthesized. Prior to storage, each emulsion was characterized in Dp and PDC, both results are shown in Figure 1.



Figure 1. Values of A) Dp and B) PDC obtained in the emulsions recently prepared as a function of Mw of PVA and their concentration at 25°C.

We can see from Figure 1A that Dp decreased when the PVA concentration was higher for each Mw of PVA used. Beside, the coloidal stability of the PLGA nanoparticles increased when the Mw of PVA and their concentration were higher as show in the Figure 1B. The behaviors observed in both figures were consistent with the reported in the literature [4].

Next step, was to store all the PLGA emulsions at  $\approx 25^{\circ}$ C in order to examine their colloidal stability. According to the results obtained for Dp and PDC, the colloidal stability of the emulsions improved with 15g/L of PVA as stabilizer, although only with the PVA of Mw= 85-124 KDa was possible to obtain an emulsion colloidaly estable (Dp and PDC values approximately constants) all the time, as can be observed in the Figure 2.



Figure 2. Evolutions of A) Dp and B) PDC in the PLGA emulsions stabilized with different PVA using a concentration of 15 g/L during storage.

This result was supported when analyzed the surface area of the PLGA nanoparticles obtained during their elaboration and the evolution of the PDC using different Mw of PVA at 9 g/L during storage, are shown in Figure 3.



Figure 3. A) Surface area of the PLGA nanoparticles obtained during their elaboration and B) PDC evolution in the PLGA emulsions using different Mw of PVA at 9 g/L during storage.

As shown in Figure 3A, the surface areas were opposite using different Mw of PVA at 3 or 15 g/L. However, was similar using a concentration of PVA at 9 g/L (empty circles). In this case, the surface area was around of S = 4,100 cm2/cm3. Due this result, Figure 3B shows the effect of Mw at 9 g/L on the PCD evolution for the three emulsions during storage. Is clear that the colloidal stability of the PLGA emulsion was higher using Mw= 85-124 KDa. This confirms that the stability observed in Figure 2 (A and B) was due to the influence of this Mw of PVA than a minor surface area in their nanoparticles, as can be observed in Figure 3A.

### Conclusions

By using ROP process to the synthesis of PLGA and emulsion-evaporation method to the elaboration of nanoparticles, was possible to prepare nine emulsions using different Mw value and concentration of PVA. According to the experimental results obtained during storage, only was possible to obtain an emulsion stable all the time using PVA= 85-124 KDa at 15 g/L. In this sense, the colloidal stability was due to the influence of this Mw of PVA than a minor surface area in their nanoparticles.

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# SELF-ASSEMBLY OF PLURONIC BLOCK COPOLYMERS IN A PROTIC IONIC LIQUID

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Nanoscale self-assembly in ionic liquids (IL) is of great interest as these fluids have special thermal and chemical stability, negligible vapor pressure, high ionic conductivity and wide electrochemical window. Using small angle neutron scattering, shear rheology, polarizing optical microscopy, and ionic conductivity measurements, we studied the self-assembly and the structure-rheological properties relationships of amphiphilic Pluronic block copolymers (triblock copolymers made of a central polypropylene oxide (PO) and two end polyethylene oxide (EO) blocks) dissolved in a protic ionic liquid (ethylammonium nitrate, EAN). Three systems were studied, namely, F127 ((EO)<sub>106</sub>(PO)<sub>70</sub>(EO)<sub>106</sub>)/EAN, P123  $((EO)_{20}(PO)_{70}(EO)_{20})/EAN,$ and L121(EO)<sub>5</sub>(PO)<sub>70</sub>(EO)<sub>5</sub>/EAN. The length of the EO block has a significant effect on the shear viscosity and elastic modulus of the micellar aggregates. Spherical micelles are formed for higher Mw EO blocks, which stabilizes the highly curved spherical interface. For lower EO Mw steric effects are less significant and the interface curvature is lowered, forming cylindrical (wormlike) micellar aggregates. Spherical micellar solutions behave as non-birefringent Newtonian liquids whereas wormlike micelles show a considerable viscoelasticity and strong flow birefringence. A comparison with pluronic self-assembly in water is interpreted with molecular thermodynamics, providing guidance for the self-assembly of non-ionic surfactants and block copolymers in ionic liquids.

## EXPERIMENTAL-THEORETICAL ANALISYS OF THE POTENTIALS SITES OF FUNCTIONALIZATION OF NPTIO2 WITH TEMPO MOLECULES

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Experimental and theoretical analysis were studied in order to determine the functionalization mechanism between TEMPO molecules and the different allotropic forms of titanium dioxide nanoparticles (NPTiO2, Anatase 101 and Rutile 110). The theoretical analysis was carried out using methods of molecular mechanics, such as method PM6 and the Density Functional Theory with the Hybrid method B3LYP at 3-21g approximation, in order to find the minimal energy and 6-31g\* to optimize the energy at minimal energy. NPTiO2: from Degussa P25(70 wt.-% anatase, 30 wt.-% rutilo), anatase (99% pureza de Aldrich) and rutile (99% de pureza de Aldrich) were used in all our studies. All theoretical results were demonstrated experimentally by X-rays photoelectron spectroscopy (XPS), FT-IR, TGA and DSC.

The results suggest that there are preferential places where it is possible to grafting TEMPO molecules on the surface of titanium dioxide. Also, we found that the binding energy between TiO2-TEMPO which forms a peroxidic bonds (O-Ti-O-O-N, peroxide) is greater on the surface of rutile than the surface of anatase. Experimentally we also calculated the density of grafting and the efficiency for the functionalization of nanoparticles TiO2 Degussa, by TGA, the results are shown in the table below

	wheight loss		graft density		
TAG	%	Gφ1	Gφ1	Gq1	% grafting
	125°-500°C	μποι/π/2	molecules/mm <sup>2</sup>	µmo⊮g	efficiency
NP-TiO2 P25	0.9745				
Grafted NP-TiO2 P25	4.41	4.15	2.5	232.4	52

Table 1: Density of grafted TEMPO molecules on the surface of Degussa P25 np-TiO2

\* efficiency was calculated using the data obtained by Muller et al.[1] where it was found that the maximun number of -OH groups per nm2 on the surface of Degussa P25 TiO2-np is 4.8 OH/nm2.

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# MECHANICAL CARACTERIZATION OF COMPOSITE MATERIALS FROM VIRGIN OR RECYCLED HDPE AND LIGNOCELLULOSIC FIBERS.

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### Abstract

In this work, lignocellulosic fibers from different sources: Agave tequilana baggasse, coir from copra's production, and wood of Jatropha curcas were used as reinforcement of PP virgin and recycled HDPE. Extrusion process was used to obtain sheet of the composite materials with PP virgin or recycled HDPE matrix, 30% w/w of fibers, 5% w/w coupling agent, and 3 or 6% w/w of processing aid. The composite show higher tensile modulus than the matrix and this attributed that the fiber have a Young's modulus that the PP virgin or HDPE recycled. The coir fibers show the better mechanical properties with value of 16 MPa and 634 MPa to tensile strength and Young's modules, respectively.

## Introduction

Pollution is nowadays a big problem witch increase doe to the enormous quantity of waste as consequences of human activities. In the big cities, plastics represents about the 8.95% weight of the municipal solid waste (MSW) [1]. Until landfills are a nice option to confine the MSW, it is require great terrains extension and, we should be able to consider the reuse some of these materials toward the obtaining of new products. In the field, agro-industrial activities generate great amounts of lignocellulosic material (branches, stems, leave, etc.), that in the majority of the cases are considered wastes, causing contamination problems in the accumulation places. The agroindustrial and agricola wastes can be a lignocellulosic fiber source. A form to reduce these contamination by this materials (besides obtaining products of added value), is the elaboration of "wood plastic composite" or WPC, this materials is obtained from recycled plastic and lignocellulosic fibers. These materials have advantages such as dimensional stability, easy processing, mechanical resistance [1]; therefore, the lignocellulosic fibers are of low cost, lower abrasive, and renewable [2, 3].

The use of thermoplastic polymers such as polyethylene (PE) and polypropylene (PP) mixed with lignocellulosic fibers to manufacture WPC materials, it has become in a new field of the investigations related with the timber industry [2]. The WPC have certain advantages against others including dimensional stability, malleability, tensile and impact strength [3], are renewable, low maintainers cots, and durability. One of the biggest challenges of this material is to optimize the content fiber/polymer trying to decrease costs and to compete with the commercial products [4, 5]. Nevertheless, the materials composed of lignocellulosic fibers and polyolefin need to be made compatible to improve their poor adhesion and its mechanical properties. Uses of coupling agents as polyolefin-g-maleic anhydride improve fiber-polyolefin adhesion [4].

This work propose obtaining wood plastic composite as an alternative reuse of plastic and lignocellulosic wastes generated in the Yucatán State and in other areas of Mexico, also contributing to the reduction in wood consumption from forest, since these materials can be wood substitute. Three different kind ok lignocellulosic waste (Coir, Agave Tequilana bagasse, and Jatropha India) and two polymers: Recycled HDPE and virgin PP were used as to obtain wood plastic composites.

Extrusion grade polypropylene was used (HP423M) of INDELPRO, with a density of 0.9 g/cm3 and a melt index of 3.8 dg / min. Recycled polyethylene was obtained from Yogurt beverage containers. Epolene Polybona and Epolene E-43 (with acid number (mg KOH / g) 45 and molecular weight of 9100 daltons) from Eastman was used as coupling agents for HDPE and PP, respectively. These materials have groups of maleic anhydride (MA) grafted onto the polymer chain. Struktol TPW113 from Struktol Company was used as processing aids. The polymers and additives were ground using a knife mill from Brabender fitted with a 1 mm mesh to separate the ground material.

Lignocellulosic fibers were obtained from fibrous waste generated during the exploitation of agroindustrial use plants. Agave fiber was obtained from tequilana agave bagasse which is a residue of the tequila, coir fiber was obtained from the coir husk which is a waste of the copra production, while Jatropha fiber was obtained by grinding the branches of India Jatropha plant whose fruits are used in the production of biodiesel. The fibers were reduced in size and sieve fraction recovered 40-60 and 60-80. Additionally, agave fibers were heated to boiling for 1 hour to remove material deposited on its surface.

## Characterization of raw materials.

The thermal properties of polymers were obtained using differential scanning calorimeter (DSC) model DSC-7 from Perkin Elmer. Samples were run under nitrogen atmosphere using a heating rate of 10 °C/min. Lignocellulosic fibers are thermally characterized using a thermogravimetric balance model TGA7 from Perkin Elmer. Samples were run under nitrogen atmosphere with a heating rate of 10 °C/min in a temperature range of 50 to 600 °C. The length and diameter of the fibers were determinate from the photographs of the fibers obtained using a stereoscope from Motic Brand.

Preparation of wood plastic composites (WPC).

The WPCs were obtained in the form of sheets (10 cm wide and 2.5 mm thick) using a twin screw extruder from Brabender, with a speed of 40 rpm and temperatures of 180 °C in the extruder and 187° C on the die. In all WPC, the fiber content was 30 wt%. The amount of coupling agent (copolymer PP-g-AM or) and a processing aid agent (fatty acids stearate) in composites with agave fibers and PP matrix, are shown in Table 1. WPC with recycled HDPE matrix were formulated with 5% coupling agent (PE-g-MA), and using percentages of processing aid agent of 3 and 6% by weight.

Table 1. PP and .	Agave Teq	uilana fiber	formulation to	obtain the wood	plastic composite.
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0	F1	F2	F3	F4	F5	F6	F7	F8
Coupling Agent	0%	2.5	5	7.5	10	7.5	7.5	7.5
Processing aid	0%	0	0	0	0	2	4	6

Characterization of wood composite materials (WPC).

The tensile properties of WPC were conducted based on ASTM D 638-02, using an Instron Universal machine with load cell of 500 N. The Type I specimens, specimens were conditioned for 48 h prior to the test at 23 °C. Micrographs were obtained from the rupture surface of the composites with scanning electron microscopy from JEOL (JSM 6360 LV model), the samples were coated with a layer of gold prior the SEM observation.

### **Results and Discussion**

Characterization of matrix and fibers.

In the DSC thermograms observed melting peaks of the polymers used as matrices. The Tm of recycled HDPE matrix was 135.7 °C and that of virgin PP was 165 °C. The TGA thermograms of lignocellulosic fibers (Figure 1) show three weight loss in the range of 50 to 700 °C. The first weight loss of 5% at a temperature of 100 °C is attributed to moisture in the fibers. The second in the range of 270 to 370 °C with a weight loss of 40 to 50% corresponds to the degradation of the hemicellulose and the start of the cellulose degradation; The DTGA thermogram show a maximum degradation between 320 to 330 °C. The third drop corresponds to the degradation of cellulose and lignin present in the fibers. It is noted that the DTGA thermograms shown an intense peak at 400 °C in the fiber of agave fibers while Jatropha and Coir fibers had wider peaks and higher temperatures. This can be attributed to these fibers have higher lignin content of agave fibers. On the other hand, coir fibers (1.61 mm long and 203 microns in diameter) showed the higher aspect ratio compared to agave (1.52 mm long and 268 microns in diameter) and Jatropha (0.62 mm and diameter of 186 microns) for the 40-80 mesh fibers retained.



Figure 1. TGA and DTGA thermograms of vegetal fibers used to obtain composite materials.

Characterization of composite materials.

Figure 2 shows the effect of coupling agent and processing aid agent on the mechanical properties of WPC with PP and agave fibers. It can be seen in Figure 2a that increasing the coupling agent content increases slightly the modulus of the WPC material with respect to the materials in which no coupling agent was used. The treated fibers showed higher modulus values than the untreated fibers which can be attributed to improved dispersion and less agglomeration of fiber, because the treatment removes low molecular weight compounds on the surface of the fibers which favors

their agglomeration. It is also noted that an increase of coupling agent results in an increase in the tensile strength of composites with up to 7.5% of coupling agent (figure 2b). This behavior is attributed to a better interaction between the matrix and the fiber due to the use of coupling agent. It has been reported that the PP-g-AM ester can form bonds with the fiber and increased fiber-matrix compatibility. It can observe a light increase in the module with the processing aid content for both materials (figure 2c). This behavior is attributed to improved dispersion of the fibers due to processing aid agent. Not effect was observed in the tensile strength due the processing aid (figure 2 d).

The effect of processing aid in composites with PE matrix and lignocellulosic fibers (coir, jatropha and agave) is shown in Figure 3. It is observed that composites with agave and coir fiber have higher values of module than the materials obtained using jatropha fibers. This could be because the first have L/D ratio greater. It is observed that an increase in the content of a processing aid results in a slight decrease in the modulus of the material when used coir fiber and agave while no effect was observed when using jatropha fibers. As noted above, the processing aid is used to reduce friction between the components of the composite material and facilitate its flow during processing.



Figure 2. Effect of the coupling agent and processing agent aid on mechanical properties of PP/Agave bagasse fiber composite materials.



Figure 3. Effect of the processing agent aid on mechanical properties of recycled HDPE/lignocellulosic fibers using 5% of the coupling agent.

Analysis of the micrographs of the rupture surface

Figure 4 shows SEM micrographs obtained of the failure surface of specimens of WPC. In WPC obtained without coupling agent (Figure 4a-d) the failure surface show fibers with smooth surfaces and holes in the matrix, indicating that the fibers are pull out from the matrix during the tensile test. This is due to the poor interaction between the fiber and the polymer matrix. The use of coupling agent improves the interaction between fiber and matrix and fibers in the failure surface (figures 4e-4h) are embedded in the matrix and polymer residues is observed on the surface of the pull out fibers.



Figure 4. SEM micrographs of the tensile fracture surface in composite material. Matrix recycled HDPE: a-c) no coupling agent, e-g) with coupling agent and processing aid. Matrix PP: d) without coupling agent, h) with coupling agent and processing aid.

## Conclusions

Composite materials of recycled or virgin polyolefins and lignocellulosic fiber were obtained. The use of coupling agent improved the compatibility between fiber and matrix increasing the mechanical properties of this material. Coir fibers showed the best mechanical properties when it was used with recycled HDPE. Low molecular weight components removal presents in Agave Tequilana fibers got itself low agglomeration in the composite material, getting higher modulus and tensile strength than that composite with non treated fibers.

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## NEW METHODOLOGY FOR THE ESTIMATION OF THE TIP BROADENING EFFECT IN AFM LATERAL MEASUREMENTS OF CELLULOSE NANOCRYSTALS

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Since its invention in the mid 1980s,[1] atomic force microscopy (AFM) has found a large number of applications, among those, is the measurement of nano- and microscale dimensions of particles and topographical features.[2] The dimensional measurements of nanostructures by AFM are impeded by tip broadening effects. The term "tip broadening effect" in AFM is related to the effects of finite stylus width on surface-contact profilometry.[3]

In the present work, a method is proposed for the estimation of the tip broadening effect in AFM width measurements of cellulose nanocrystals (CNCs). The method is based on the first and second derivatives of the apparent transverse height profiles of the non-spherical nanoparticles. The method is explained for cylindrical and elliptic cylindrical nanoparticles on simulated AFM height profiles and experimentally demonstrated on gold nanorods of known dimensions. Application of the method to CNCs prepared from the sulfuric acid hydrolysis of alpha-cellulose, gave an actual average width of about 11.8 nm and a width-to-height ratio of 2.7. The estimated actual width of the particles was independent of tip radius. The magnitude of tip broadening decreased with decreasing tip radius and was constant within a sample. The accuracy of the method depended on the spacing of the data points in the height profile. The fact that the magnitude of tip broadening was constant within a sample indicated that, once determined from a small number of particles, it could be used to correct the apparent width and length values of all particles within the sample for tip broadening.

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# THE ROLE OF LOW MOLECULAR WEIGHT SULFONATED POLYSTYRENE IN ESTABLISHING A UNIQUE HIGHLY STABLE AQUEOUS FERROFLUID

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### Abstract

One of the most optically transparent magnetic materials known at room temperature consists of nanocrystalline  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> dispersed in a DVB cross-linked sulfonated polystyrene (pss) matrix [1,3,4]. When attrited in water or methanol without surfactant and subsequently processed by centrifugation and ultrafiltration, the nanocomposite leads to a highly stable, low optical density ferrofluid [2] with unique properties and uses in a variety of applications [5,6]. Despite the scientific and technical value of the ferrofluid, including its role in allowing for free-rotor nanomagnets in the solid state [8,9], the nature of the sulfonated polystyrene that leads to the highly stable aqueous iron oxide ferrolfuid (ζ-potential = -82 mv) remains undetermined [7]. A brief historical perspective and review of the characteristics of the low optical density magnetic (LODM) solid and liquid materials are presented along with results that shed light on the nature of the sulfonated polystyrene that caps the iron oxide nanoparticles to form the high stability colloid. Attempts to synthesize the same ferrofluid using a bottom-up process using ex situ generated iron oxide nanoparticles followed by the addition of commercially available sodium poly(styrene sulfonate) of different molecular weights have failed. Moreover, the synthesis of decigram quantities of the free-rotor magnetic nanocomposite material that results from the methanol ferrofluids has been difficult to accomplish and at times, even difficult to reproduce. The average molecular weight and molecular weight distributions of the PSS polymers in ten different ferrofluids prepared by the attrition of LODM resins were determined using GPC/SEC techniques. Results suggest a tri-modal molar mass distribution in the 1,000 to 100,000 range.

### **Historical Perspective and Summary**

Commercially available divinylbenzene cross-linked cation exchange resins of poly(styrene sulfonate) can be used to make composites containing crystalline maghemite,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, in the nanometer range. These nanocomposites constitute one of the most optically transparent room temperature magnetic materials known [1]. Their synthesis is schematically illustrated in Fig. 1<sup>\*\*</sup> and is a cyclic process where additional particles of the oxide are produced in each cycle or loading, presumably at nano-reactor sites throughout the cross-linked resin, where the matrix mediates the synthesis. The general characteristics and magnetic and optical properties of the nanocompoaites can be found in references 1 through 6. The transparency of the maghemite-loaded solid resin beads (~ 400 mesh) with a magnetic saturation moment of about 6 emu/g at room temperature can be seen in Fig. 2a. Figure 2b shows a TEM image of a cross section of the beads with particle diameters averaging between 8 and 10 nm. The salient magnetic and optical properties of a once-loaded bead and of the nanoscale  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, are shown in Figs. 3a and b, respectively. The composites are superparamagnetic, while nanoscale  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> has an extinction coefficient about an order of magnitude less than that of the bulk form and a red-shifted absorption edge. The latter effects are quantum related.

The magnetic composite, when roll milled or attrited in a planetary mill, dry or wet, breaks down to form a powder. The higher the loading of oxide, the more easily the resin breaks down from internal strain associated with the increase in particle density. When milled in a liquid, the solid nanocomposite forms a ferrofluid possessing similar magnetic and optical properties as those of the solid. Ferrofluids possessing room temperature magnetic saturation moments higher than 35 emu/g have been achieved by milling multiply loaded composites. When the original sodium counter ions in the pss resin are replaced by Li, K, Rb or Cs ions, the absorption edge shifts further, markedly affecting the fluid's optical properties. These magnetic aqueous colloids are stearically stabilized as opposed to the ionically stabilized ferrofuids with

relatively short lifetimes and possess a  $\zeta$ -potential of -82 mv; shelf lives can be in excess of 30 yrs. The ferrofluids have been used to form colored magnetic materials by mixing or blending with appropriate pigments or dyes and can also form free standing films or films on a multitude of substrates either neat, or in combination with water or alcohol soluble polymers [5,6]. The first *internal* Gibbs-Marangoni effect measurements on a liquid magnetically suspended in a microgravity environment were successfully conducted by the European Space Agency using the low optical density ferrofluid.

When the magnetic nanocomposites are milled in methanol, they form thixotropic colloids as distinguished from their aqueous forms. The optical and magnetic properties remain similar or identical to those of the aqueous ferrofluids. However, when frozen at 200°K, and subjected to a few  $\pm$ - oscillations of a magnetic field of ~ 1T, the methanol ferrofluid forms a methanol polymer composite that leads to the first known example of a solid composite where the nanoparticles are free to rotate in the matrix when subjected to the torque of an applied magnetic field [8,9]. The magnetic behavior is illustrated in Fig 4a<sup>\*\*</sup>, and is observed down to  $4.2^{\circ}$ K. The preparation and recyclability of the free rotor material from liquid to solid to liquid is shown in Fig 4b. A schematic representation of the free rotor material, first in the fixed sate, then randomly free in an oscillating field after magnetic annealing, then aligned in an applied magnetic field is shown in Fig 5a. The M vs H magnetic behavior of the mechanically matrixfixed particle compared to that of the free rotor is illustrate in Fig 5b. In the case of the fixed rotor, he material shows superparamagnetic (SPM) behavior above the blocking temperature and hysteresis below the blocking temperature. When the particles become free to rotate (right side plot), the magnetic behavior is bi-stable, and in the idealized state has one value either plus or minus. The free rotor material thus behaves as a switch and, in principle, can act as a three dimensional nanocompass and as an attitude sensor at the nanoscale. Moreover, the material, applied as an electrical transformer core material, would, in principle, be virtually eddy-less and have minimum heat loss since the rotors follow the direction of the field. The physics of the free rotor has recently been modeled [10].



Figure 1. Schematic illustration of multicycle solid nanocomposite generation.



Figure 2. (a) γ-Fe<sub>2</sub>O<sub>3</sub> loaded resin beads (400 mesh) illustrating optical transparency; (b) TEM image of bead cross section.

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Figure 3. (a) M vs H/T plot showing SPM behavior of solid γ-Fe<sub>2</sub>O<sub>3</sub> nanocomposite; (b) optical absorption coeficient of nanoscopic ('mesoscopic') γ-Fe<sub>2</sub>O<sub>3</sub> vs. bulk.



Figure 4. (a) M vs H plot showing free rotor behavior (see ref. 8 for explanation); (b) overall preparation and behavior of the free rotor material upon cooling and magnetic field exposure.



Figure 5. (a) a schematic of the γ-Fe<sub>2</sub>O<sub>3</sub> nanocomposite in the particle-fixed vs free state and aligned by an applied field; (b) M vs H magnetic behavior of the SPM behavior of the particles in the fixed state above and below the blocking tmeperature (left side) and of the SPM free and hysteresis free magnetic behavior of the nanomagnet rotors (right), which display two-state switching behavior.

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The mechanism of free rotor formation at the molecular level is unknown [7]. The present model is one involving a core shell type structure and is based on data that are consistent with hydrogel formation and behavior. In the magnetically unannealed, particle-fixed state, hydrogen bonding between particle and matrix is thought to play a controlling role [8]. Upon application of a magnetic torque, hydrogen bond breaking is believed to occur with possible conformational changes in the methanol polymer matrix that lead instead to a hydrophobic cavity wall. In this study, the average molecular weight and molecular weight distributions of the pss polymers in ten different ferrofluids prepared by the attrition of LODM resins were determined using GPC/SEC techniques to shed some light on the nature of the polymers responsible for the formation and stability of the aforementioned ferrofluids.

## Experimental

## GPC sample preparation and analysis

Ten samples from different preparations of ferrofluids all containing sulfonated polystyrene (PSS) were subjected to digestion of the iron oxide nanoparticles with a 1:1 aqueous mixture of 0.1 molar HCl and 0.15 molar oxalic acid at which the dispersion turns to a solution. Sample concentrations for GPS analysis were adjusted to contain ~ 1 mg of polymer per ml of solution. The solutions as prepared were transferred to an auto-sampler vial and measured with an Agilent 1100 series HPLC at PSS Polymer Standards Service, GmbH, Mainz, Germany. Polystyrene sulfonate (pss) standards with different molecular weight were used for calibration. The calculation of the average molecular weights and the molecular weight distribution of the samples was done by the so called slice by slice method based on the pss calibrations. The eluent was 11.88 Na<sub>2</sub>HPO<sub>4</sub> g/L aqueous solutions with PSS MCX columns: 10µm, 100 Å, ID 8.0 mm x 300 mm; and 10µm and 1000 Å, ID 8.0 mm x 300 mm. An Agilent 1100 HPLC-Pump at 1.0 ml/min with Agilent 1100 auto-sampler with 20 µl inject volume were used in the analysis.

### **Results and Discussions**

The results of the GPC study suggest a tri-modal molar mass distribution for the pss polymers in the 1,000, 10,000 and 100,000 range as shown Fig. 6. The different colors represent different ferrofluids, all in the digested state where the iron oxide particles were converted to soluble Fe(III) ions to free any associated polymer. Fig. 6a represents ferrofluids that received no ultrafiltration and subsequently where not of the quality of those that did (Fig. 6b). The ferrofluids in Fig. 6b possessed the characteristics of the ferrofluids described above. The one exception in Fig. 6b is the ferrofluid represented by the light blue or turquoise color. That particular ferrofluid was highly viscous and showed signs of polymerization over a 30 yr period. The eluent curves showed that that particular ferrofluid consisted mainly of a very high fraction of the high molar mass polymer. The ferrofluid's stability and magnetism over the years appeared to be unaffected and there were no signs of sedimentation in the sample container. No significance has been assigned to the low intensity midrange molar mass distributions pending further analysis. The lower molar mass distributions in the 1,000 range are possible oligomeric or low molecular mass poly(styrene sulfonate) that may be the effective surfactant or capping agent responsible for the formation, stability and performance of the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> pss ferrofluids. The lowest molar mass peaks appear to be a consequence of the eluent and reagents used to digest the iron oxide particles. Elemental analysis of the dried ferrofluids and their solid state progenitors show only C, H, O, S, and Fe. IR, Raman, UV-Vis, mass spectrometry and other data are all consistent with the a poly(styrene sulfonate) composition.



Figure 6. Molar mass distributions for ten ferrofluids in the digested state; (a) no ultrafiltration; (b) with ultrafiltration.

### Conclusions

GPC/SEC analysis techniques of poly(styrene sulfonate) stabilized frrofluids of nanocrytalline  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> show a tri-modal molar mass distribution in the 1,000 to 100,000 range and suggest possible stabilization of the iron oxide by low molar mass polymer in the 1,000 range, following the degradation of original DVB cross-linked pss resin by attrition. A full investigation of the polymer content of the ferrofluids is underway to determine the species responsible for the formation, stability and performance of the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> pss ferrofluids as well as for the production of the ferrofluids from a one step bottom up rather than from the two step bottom up to top down approach currently in use.

### Acknowledgments

<sup>\*\*</sup>Figures 1 through 3 from reference 1, by permission; figures 4 and 5b from reference 8 by permission. We thank PROLEC GE, Apodaca, Nuevo León, México for their generous support 2008-10.

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# ATOM TRANSFER RADICAL POLIMERIZATION OF ACRYLIC MONOMERS ON THE SURFACE OF SINGLE WALLED CARBON NANOTUBES

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## Abstract

After the discovery of carbon nanotubes in 1991 by Iijima [1] a lot of scientific work has been realized with the main aim to understand and characterize their properties and find new applications in medical, biological and mechanical fields including the preparation of electronic materials [2, 3]. Unfortunately, Single Walled Carbon Nanotubes (SWCNT) have a great disadvantage, they are highly hydrophobic and can't be moisturized by protic solvents, giving as a result poor solubility in most organic solvents. For that reason they cannot be fully integrated in most organic materials, i.e. polymers, because of the lack of interfacial interactions on the surface of the SWCNT. In the present communication we describe the surface modification of the SWCNT with 4-hidroxyethyl-pheny group [PhCH2CH2OH]. Once reacted, this chemically attached group was further modified with 2-bromoisobutiryl bromide to get an ATRP initiator. The versatility of the methodology is interesting because the overall modification reactions reach the 90% yield. Acrylic monomers were polymerized in high yields using the prepared modified-SWCNT and structural properties of all compounds were studied.

## Introduction

The term nanotechnology can be defined as the study, creation, manipulation and application of materials, devices, and systems through the control of matter at nanometer scale, i.e. at the level of atoms and molecules. In recent years, this field has been developed extensively, and has achieved great importance in science.

In research areas such as the development of nanostructures, carbon nanotubes are largely studied because of the extensive potential applications in plenty of materials, due to their physical and chemical properties [4]

Carbon nanotubes (CNT) are an allotropic form of carbon with cylindrical structure, which belong to the family of Fullerenes. These cylindrical molecules have novel properties that make them potentially useful in many applications in the field of nanotechnology, electronics, optics and other fields of materials science. These materials have been applied, in the storage of hydrogen, in field emission and electronic devices, devices for nanofluids and interconnectors, etc. In addition they have been used to reinforce materials such as cements, paints and polymers, with the aim of increase its resistance. In the last years, CNT have been extensively employed as reinforcement material in polymers, generating materials with improved mechanical, electrical and thermal performance. Nanotubes are classified depending on the number of carbon layers by which are formed, if they possess only a single layer of graphite, is called simple wall, (Single Walled Carbon Nanotubes, SWCNT) nanotubes, and if they are formed by two or more layers of graphite are named nanotubes of multiple wall, MWCNTs (Multi Walled Carbon Nanotubes).

The CNT have excellent mechanical, thermal and electrical properties, which have been utilized to improve the properties of different types of materials. CNTs are well known for possessing high thermal conductivity and high strength tensile. These materials transport the electric current more effectively than the traditional copper wires, and in addition, the CNT dissipate the heat more efficiently [5].

Nanotubes are composed of hexagons, pentagons and heptagons rings, and depending on the diameter and chirality of these rings, they can be considered as conductor or semiconductor materials. Nanotubes with metallic character (type armchair), exhibit very high electrical conductivity. It is estimated that CNT can carry a trillion of amperes per square centimeter, which is more than the traditional copper wires can transport [6]. A wire of copper fails when is used to transport a million amperes per square centimeter since the heat generated by the electric current fuses the cable.

However, CNTs experiment a lack of solubility in organic solvents and aqueous solutions because of the strong Van der Waals interactions that cause the formation of agglomerates. In addition, due to the small particle size, handling and processing is difficult for CNTs. To minimize these disadvantages, nanotubes can lead chemical reactions on its structure to introduce functional groups that can make them more soluble to be easily incorporated into different type of materials preserving its original properties [7].

The covalent functionalization is a very promising methodology to improve the performance of the CNT with the improvement of dispersion and solubility, as well as the creation of novel composites materials. The covalent functionalization is the reaction of the lateral wall of the nanotubes with certain specific chemical reagents generating the formation of covalent bonds. This type of functionalization has been widely studied, generating an important set of data useful in the graft reactions with different chemical groups to the surface of the nanotubes. One of the problems of the covalent additions is that treatment of CNTs under extreme conditions, as it is the use of acids, can cause damage to the structure of nanotubes and its properties. For that reason it is necessary to develop methods of modification which can be able to preserve the original properties of these materials. Here we report the surface modification of the SWCNT with 4-hidroxyethylphenyl group [PhCH2CH2OH]. This group is further modified with 2-bromoisobutiryl bromide to get an ATRP initiator. The versatility of the methodology is interesting because the overall modification reactions reaches the 90% yield. Acrylic monomers were polymerized in high yields using this modified-SWCNT. Structural properties of all compounds were studied by, TGA, CP-MAS NMR, FTIR, and TEM

## Experimental

Polymerization of PMMA on the surface of the SWCNT. 0.22 mmol of cooper bromide (I) and 0.264 mmol of hexamethylentetramine dissolved in phenylether were placed in a 100 mL Schlenk type flask under inert atmosphere. The solution was stirred for 30 minutes, to ensure the formation

of the complex Cu(I)/HMTETA. After this time, the monomer MMA (150 mmol) was added slowly dropwise to the flask. The SWNT-initator was suspended in 20 mL of phenylether, and this solution was sonicated for 30 minutes. Then, this solution was added to the flask, the reaction mixture was degassed by three freeze-thaw cycles with liquid nitrogen. The flask was placed in a thermostated oil bath at 75°C for 120 minutes. After the reaction time was completed, the product was dispersed in THF, and precipitated in hexanes, to recover a black solid, wich was dried overnight under vacuum at 40°C. Whit this procedure the product SWNT-PMMA was obtained. After the surface modification of SWCNTs with poly(methyl methacrylate) [Mn = 9,866, 91%]w/w of polymer contained in 6.5% w/w of the SWCNT] this nanocomposite was mixed with (PMMA) through the method known as melt mixing. Previously to the mixture the components were dried in vaccum for 12 hours at 70°C, in order to eliminate the moisture that might be present in the polymer matrix. Once the material was dried, the next step consisted of the physical mixing of the two components followed by melt mixing using a laboratory Dynisco mixer-extruder series LME. PMMA-SWCNT nanocomposites were homogenized using an extruder, were temperature was set at 190°C at the feeding and mixing sections. At the end, an ultrasound horn was connected, which operates at 19.09 MHz and the temperature was set at 180 °C. The residence time of the material in the extruder was 8 minutes. The preparation of these nanocomposites was done at three different concentrations for SWNTs-f-PMMA were used, being: 0.1, 0.3 and 0.5%, w/w using in all of them the same amount of PMMA (70 g).

### **Results and Discussion**

Surface modification of the SWCNT with 4-hydroxyethyl-phenyl group [PhCH2CH2OH] can be obtained by the reaction between 4-(1-hydroxyethyl)aminobenzene and isopenthyl nitrite. The characterization of these modified SWCNT surface with the 4-(1-hydroxyethyl)-phenylidene group was carried out by FT-IR were the characteristic band at 3342 cm-1 corresponding to the stretch of the O-H bond of the alcohol group was found. Analysis of this compound by the hyphenated TGA-MS technique, showed a 5.6% weight loss in the range of 100 to 150°C. Also a weight loss of 15.80% at 180-250°C range was found, which has a mass peak at 92 and 91 m/s. With this evidence we propose the mechanism of thermolysis which includes the first loss of a molecule of methanol followed by the loss of a molecule of toluene. SWCNT surface modified with the 4-(1-hydroxyethyl)-phenylidene was further modified with 2-bromo-2-methylpropanoyl bromide to get an ATRP initiator.

FT-IR analysis was performed to assure the presence of the initiator molecule on the surface of the SWCNT. The spectrum showed a band at 1721.22 cm-1 corresponding to the stretch of the carbonyl group in the propanoate moiety. Additionally, several stretching bands at 1091-1155.48 cm-1, thathat correspond to the C-O bond of the hydroxyethyl group were observed. With all this results it was determined that functionalization on the sidewall of the SWNT with the group 4-(2-bromo-2-methylpropanoate of 1-hidroxyethyl) phenylidene was performed successfully.

The versatility of the methodology is interesting because the overall modification reaction reaches the 90% yield. In order to probe the ability of this new material over the polymerization of acrylic monomers, methyl methacrylate was polymerized using the SWCNT modified in the surface with the ATRP initiator.



Figure 1. ATRP polymerization of MMA on the surface of the SWCNT

For the polymerization of the MMA a modified SWCNT containing 27% w/w of the 4-(2-bromo-2methylpropanoate of 1-hydroxyethyl) phenylidene group was employed. The initiator concentration was accurate determined by TGA analysis and used to determine the monomer:initiator ratio. Also, the complex generated from the reaction between 1,1,4,7,10,10-hexamethyltriethylenetetramine and cuprous bromide (CuBr) in diphenylether as solvent at 75°C was considered. In Table 1 can be appreciated the molar ratios used in the polymerization of MMA.

Table 1. Surface polymerization of MMA in SWCNT.

Monomer	[M]	[HMTETA]	[I]o	CuBr	Yield (%)	Mn † (g/mol)	Polymer (%)*	SWCNT (%)*
Methyl methacrylate	71	1	1	1	58	4,094	81	14
Methyl methacrylate	205	1	1	1	50	9,866	91	6.5

† Determined form the TGA analysis.

One of the principal aims of the work, is to prove the utility of the initiator in the polymerization of MMA and because of that reason, different molar ratios between the monomer and initiator were selected in order to find the versatility of the ATRP initiator. In such case, if the polymerization is carried out in controlled conditions, the polymer chain length on the surface of the SWCNT would also be controlled. According to the results shown in Table 1, at the employed experimental conditions, for the polymerization of the MMA with different tested molar ratios, the maximum yield was around 58%. An efficient controlled radical polymerization must follow a first order kinetics monitored by the consumption of the monomer, a linear behavior between the increment in molecular weight with the increment in the conversion, narrow dispersity, and control over the molecular weight.

Due to the problems attached to the manipulation of these compounds, unfortunately the molecular weight cannot be evaluated directly by GPC as normally proceeds with polymers, since in this case; the polymer is covalently bonded to the SWCNT. To determine de molecular weight, the nanocompound must by hydrolized, however, this procedure is not certain at all since both the initiator and the polymer have the same type of chemical bonds and the hydrolysis of the acrylic polymer will reduce the molecular weight. Molecular weight can be calculated from the TGA analysis if the concentration of initiator chemically attached to the surface of the nanotube is known. This data had been given on Table 1, where is possible to deduct that a controlled polymerization has proceed since the initiation factor (f) is near to 1, which is defined as the ratio between expected molecular weight divided by the experimental molecular weight of the obtained polymer. This is an important data and can be considered as a measure of a controlled polymerization mechanism.

Characterization of the SWCNT-f-MMA was performed by FT-IR spectroscopy using a micro-ATR device, where a strong absorption band was observed at 1726 cm-1 which corresponds to the stretch of
the carbonyl in the ester group. In addition, a strong band appears at 1100 cm-1 corresponding to the stretch of the C-O bond of the methoxy group.

Thermogravimetric analysis of the nanocomposites obtained, showed the results on Table 2.

Experiment	MMA (%)	ATRP Initiator (%)	SWCNT (%)
1	81	5.13	14
2	91	2.43	6.5

As can be deducted from Table 2 and Figure 2 (TGA corresponding to the second experiment), there exists enough evidence to assume that the polymerization reaction of MMA on the surface of the SWCNT was successfully performed under a controlled mechanism.



Figure 2. TGA of the composite SWCNT fuctionalized with poly(methyl methacrylate).

The prepared nanocomposites can be applied as a polymeric compatibilizers agent with a poly(methyl methacrylate), to improve its mechanical, thermal or electrical properties. To evaluate this assumption, mixtures of nanocomposites and poly(methylmethacrylate) with average molecular weight (120,000 g/mol) were prepared.

A blank sample of PMMA and another one containing SWCNT in PMMA were dispersed using a lab mixer-extruder Dynisco series LME. This equipment has three main areas: feeding, mixing and output section. Ultrasound horn, was attached at the output section which helps to achieve a good dispersion of carbon nanotubes. The temperatures employed were 190°C for the feeding and mixing sections and 180°C in the output with a frequency of the ultrasound fixed at 19.09 mHz.

The material was processed with a residence time of 10 minutes, after leaving the extruder, the samples were suddenly cooled with a water bath at 4  $^{\circ}$  C. The recovered material was subjected to heat at 204 $^{\circ}$ C in plates of 0.1 mm thick and hydraulic pressure of 30 tons. The plates obtained were cut and machined to obtain the test probes according to the ASTM D-638-10.

Mechanical properties of the mixtures were studied in a SFM-120 Universal machine equipped with a gage 2 inches length with separation between clamps of 4.5 inches and test speed of 0.2 inches/minute. The environmental conditions for testing were  $22^{\circ}$ C and 51% of relative humidity. Prior to the

conduction of the mechanical test, the probes type 1 were conditioned according to the ASTM D-618-08 staying 48 hours at  $23\pm2$  ° C with a relative humidity of  $50\pm5$  %.

The mechanical properties were tested by measuring the strength at rupture, which values were registred and graphed vs the strain for the mixtures of 0.1, 0.3 and 0.5% (w/w) of modified single-wall nanotubes and PMMA (Figure 3). With this data the Young modulus was calculated and is reported on the Table 2.



Figure 3 Stress vs Strain for the mixtures of SWCNT-f-PMMA and PMMA

As it can be seen with the addition of SWCNT-PMMA to the PMMA matrix in all three cases, there exists an increase in the modulus meaning that for all cases stiffness increases as the ability of warp material decreases.

Table 3 Mechanical	properties for the	nanocompounds	PMMA/SWCN	Ts-f-PMMA.
	P - P			

ID	Strength (N)	Modulus	Stress	Strain
		(GPa)	(MPa)	(%)
PMMA (Mn=120,000g/mol)	1,663	2.34	59.19	2.71
PMMA/SWCNTs 0.1%-f-PMMA	1,116	2.87	41.98	1.53
PMMA/SWCNTs 0.3%-f-PMMA	960	2.94	35.68	1.27
PMMA/SWCNTs 0.5%-f-PMMA	983	2.95	39.95	1.5

In addition to the discussion of the mechanical properties, an increase in the Young modulus in an average 20% was found even at the smaller concentration (0.1% w/w) of SWCNT. Clear reduction in the strength (required for the rupture) of the materials and strain were obtained for all cases. With these data, it can be assumed that the main effect (in the mechanical properties) of the SWCNT in the PMMA is the increase in the rigid character of the polymer matrix reducing the strain (at list 45% with the addition of 0.5% w/w SWCNT-PMMA) and the strength (reduction of 40% with the addition of 0.5% w/w SWCNT-PMMA).

# Conclusions

The funcionalization on the sidewall of SWCNT with 4-(2-bromo-2-methylpropanoate of 1hydroxyethyl) phenylidene group was achieved in high reaction yield. This new nanocomposite material is able to initiate the polymerization of MMA by ATRP under a controlled mechanism. The content of the polymer placed over the SWCNT surface can be controlled by changing the monomer:initiator ratio. Determination of molecular weight and functionalization was determined by TGA.

When the nanocomposite containing 91% of PMMA and 5.6% of SWCNT was mixed with homopolymer of PMMA (Mn = 120,000 g/mol) in 0.1, 0.3 and 0.5% w/w to analyze mechanical properties, and increase in the rigid character of the polymer matrix with reduction of the strain was found. Strain was diminished at list 45% and strength 40% both of them with the addition of 0.5% w/w SWCNT-PMMA. Additionally Young modulus was increased 26% at the same experimental conditions.

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# NANOCOMPOSITES OF POLYMERS COMPOUNDED WITH C NANOTUBES: EFFECTS ON CRYSTALLIZATION, CROSS-LINKING, VISCOELASTICITY AND DEVELOPMENT OF ULTIMATE PROPERTIES

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Challenges in processing of polymers incorporated with carbon nanotubes (nanocomposites) prevent their wider utilization. Nanotubes introduce changes in crystallinity and crystalline morphologies for semi-crystalline polymers and alter the rates of curing for thermosetting polymers. Various properties including the viscoelasticity, swelling behavior, and flammability of shaped PNCs are intimately related to dispersion of nanoinclusions. Here compounding of nanotubes into poly(butylene terephthalate), poly(ether ether ketone), poly(vinylidene fluoride), Nylon 11, poly(ethylene glycol monoacrylate) and epoxies and the development of structure and ultimate properties of the resulting PNCs will be presented.

# EARLY NUCLEATION STAGE OF AROMATIC POLYESTERS (PET, PBT AND PEN) ON SINGLE WALLED CARBON NANOTUBES

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Understanding of nucleation in semicrystalline polymers has been a main issue in polymer physics since nucleation is the formation of the smallest crystalline entity and consequently governs the microstructure, properties and applications of polymer materials. Recently, nanoparticles have been introduced as nucleating agents resulting in better properties mainly due to their particular characteristics and strong interfacial interactions [1]. Many research groups have studied the microstructure of polymer nanocomposites based on thermoplastic semi-aromatic polyesters such as poly(ethylene terephthalate) (PET), poly(butylene terephthalate) (PBT), and poly(ethylene naphthalate) (PEN) due to their outstanding properties and competitive advantages [2, 3]. Nevertheless, the nature of chain deposition has not been revealed.

In this work we studied highly diluted PET/SWCNT, PBT/SWCNT, and PEN/SWCNT systems in order to obtain evidence of first adsorbed chains on carbon nanotubes and understand the nature of chains deposition. Transmission Electron Microscopy (TEM) observations showed that PET chains wrap the nanotubes in a helical fashion similar to some biomacromolecules. In the case of PBT, TEM images show the formation of subglobules which may serve as nuclei for the growth of crystal lamellae. Besides, in the case of PEN, morphology is close to a shish-kebab but Fourier Transformed (FFT) of TEM show no evidence of crystalline morphology. Differences in polyester morphologies may attribute to the flexibility of chains and the self-assembly of aromatic rings on hexagonal lattice of the nanotube. Additionally, we suggest a mechanism for the adsorption of PET, PBT, and PEN on nanotubes and the possibility of epitaxial nucleation is also analyzed.

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# NANOCOMPOSITES BASED ON COMPATIBILIZED PE/EVA/CLAY/FLAME RETARDANT SYSTEMS

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# Abstract

In this work, the effect of EVA grafted with maleic anhydride (EVAgMA) and PE grafted with 2-[2(dimetilamino) ethoxy] ethanol (PEgDMAE) as compatibilizers for crosslinked PE/EVA/Metalic hydroxide/Nanoclay systems was studied. The effect of these compatibilizers on physical-mechanical and flame retardant properties was also established. Nano magnesium hydroxide and two types of organomodified nanoclays were used. An enhancement on mechanical and flame retardance properties were observed in systems with Magnesium Hydroxide (MH) at 30 % as flame retardant and Nanoclay C20A at 6 %, using PEgDAME as compatibilizer. This was attributed to a synergistic effect between flame retardant and nanoclay, favored by the good dispersion of nanoparticles promoted for the compatibilizer agent and the efficiency of the crosslinked grade. In addition some of these systems could be classified as V-0 for the UL-94 standard, which is a high classification on flame retardance.

# Introduction

Poliolefins are widely used in the wire and cable industry because they offer a good balance between performance and cost, easy processability and good mechanical and physical properties. Nevertheless, the incorporation of flame retardant compounds is required to improve their flame retardance behavior. Since the most effective flame retardants are based on halogenated compounds, and because of their high toxicity, several studies have been focused on strategies to avoid the use of this type of flame retardants. The use of nanoclays with different compatibilizers [1-3], metallic hydroxides [4-6] and combinations of both [7] have been reported as non halogenated flame retardants. The organoclays influence flame retardant properties due to their high aspect ratio that increases the gas barrier property by preventing oxygen to pass freely into the flame spread material and generate a carbonaceous layer that covers the material preventing leakage.

The metal hydroxides works either in the condensed phase as in the gas phase following the endothermic decomposition with water release, reducing the temperature of the material and the surrounding gas phase [8]. However, the high loads of metal hydroxide required to improve flame resistance (up to 60%), produced a deterioration in the mechanical properties of the polymer due to low compatibility between it and the filler. To improve compatibility, compatibilizers may be added to improve the interfacial adhesion between the two, having a great effect on the mechanical properties of nanocomposite. Recently, there have been numerous studies focusing on amine-modified polyolefins as compatibilizers in polyolefin-nanoclay nanocomposites [9-11], but have not been used to improve the interactions polymer-flame retardant. Therefore, PEgDMAE theoretically could interact with the hydroxyl groups of clay and flame retardants decreasing their interfacial energy and improving their dispersion in the polymer matrix. On the hand, according to some studies [5, 12] the crosslinking of PE/EVA blends, helps to improve polymer-filler interactions, allowing the mixture to absorb larger amounts of load compared with systems without cross-linking.

# Experimental

A low-density polyethylene (LDPE) PX 20 020-P of Pemex and a copolymer of ethylene vinyl acetate (EVA) ELVAX 260 from Dupont with 28% VA were used. Two types of compatibilizers were used, EVAgMA Bynel 3095 from DuPont and PEgDMAE obtained from PEgMA Fusabond E MB-226DE of DuPont. The organomodified Nanoclays used in the study were Cloisite 20A (N-di-methyl dihydro-di-tallow ammonium chloride) provided by Southern Clay Products Inc. and Nanomer I28E (N-octadecyl amine trimetyl chloride) provided by Nanocor Inc. The flame retardant used was magnesium hydroxide (Mg (OH)2 provided by Nanostructures and Amorphous Materials Inc. with a 15 nm size. The crosslinking agent used was Di-[2-tert-butilperoxiisopropil)] benzene (Luperox 802) provided by Acros Organics.

Preparation nanocomposites.

Nanocomposites were prepared according to the formulations shown in Table 1. The compatibilizer to clay ratio was 3:1, and the ratio PE / EVA was 75/25. The peroxide content was 4.5 wt%.

Formulation	PEgDMAE	EVAgMA	<b>I28E</b>	C20A	MH	PE/EVA
PE/EVA-P	0	0	0	0	0	100
PE/EVA/C20-6	0	0	0	6	0	94
PE/EVA/I28-6	0	0	6	0	0	94
PE/EVA/MH-20	0	0	0	0	20	80
PE/EVA/PEgDMAE/I28-6/MH-30	18	0	6	0	30	46
PE/EVA/PEgDMAE/I28-6/MH-40	18	0	6	0	40	36
PE/EVA/PEgDMAE/C20-6/MH-30	18	0	0	6	30	46
PE/EVA/PEgDMAE/C20-6/MH-40	18	0	0	6	40	36
PE/EVA/EVAgMA/I28-6/MH-30	0	18	6	0	30	46
PE/EVA/EVAgMA/I28-6/MH-40	0	18	6	0	40	36
PE/EVA/EVAgMA/C20-6/MH-30	0	18	0	6	30	46
PE/EVA/EVAgMA/C20-6/MH-40	0	18	0	6	40	36

Table	1. (	Comi	position	of Na	anocom	posites
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A Henschel mixer at 1000 rpm was used for previous physical mixing, which was fed to an corotating twin screw ZSK 30 Werner & Pfleinderer extruder operating at 165 ° C and 100 rpm. Subsequently the mixture was lead to a Banbury type mixer (Brabender) with at 60-100 ° C and 50 rpm in which the crosslinking agent (peroxide) was incorporated. Finally, crosslinked plaques were prepared using a hydraulic press at 185 ° C for 15 minutes. Samples were then characterized by XRD diffraction to assess the evolution of d001 reflection angle. Flame resistance was performed according to vertical UL-94 test using CEAST flammability chamber and mechanical resistance tests were performed according to ASTM D-638.

# **Results and Discussion**

X-ray diffraction (WAXD)

Figure 1 shows the diffraction patterns of nanoclay (I28E) and nanocomposites with magnesium hydroxide (MH), with PEgDMAE and EVAgMA as compatibilizers. EVAgMA compatibilizer

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show small shoulders at lower angles, indicating an intercalated nanocomposite. In the case of PEgDMAE,  $d_{001}$  plane peak attributed to an ordered structure disappears, indicating the formation of an intercalated-exfoliated nanocomposite, as a result of better interaction between the amine groups with the hydroxyl groups of MH and clay. C20A clay composites (Figure 2) show a similar trend: better dispersion with PEgDMAE and higher reduction on the signal of d001 plane as compared with the I28E clay. This can be observed when comparing both intensities in figures 1 and 2. It has also been reported that an adequate dispersion of MH in the matrix directly affects the dispersion of nanoclay [9]. For both clays, PEgDMAE compatibilizer helps the formation of exfoliated nanocomposites more easily than EVAgMA.



/ EVA I28E clay (6%) and MH.

Figure 1. XRD patterns of nanocomposite PE Figure 2. XRD patterns of nanocomposite PE / EVA C20A clay (6%) and MH.

#### Flame resistance

The results of the UL-94 test for nanocomposites are shown in Table 2. Reference samples, PE/EVA, PE/EVA/MH and PE/EVA/Clay could not be classified according to UL-94. In the case of PE/EVA/flame retardant drip occurs during the test Figure 3 (a), because the flame retardant itself does not form a carbonaceous layer that protects the material, so when burned it fails to maintain the shape. In PE/EVA/Clay samples no dripping was observed, this mainly due to the formation of carbonaceous layer by the clay, as shown in Figure 3 (b). According to the results of WAXD, we see that for I28E clay with EVAgMA compatibilizer, clay has a lower dispersion (Figure 1) avoiding that this material enters V-0 classification of flame retardance. Table 2 and figures 4 and 5 shows the flame results for the samples of PEgDMAE compatibilizer, containing 30% of MH that achieved V-0 classification. This indicates that PEgDMAE compatibilizer forms a more intercalated-exfoliated compound, with both I28E and C20A clays. This positively influences the flame retardance behavior and that the nano size of the filler produces good results in the classification using lower content of flame retardant agent. In the case of EVAgMA compatibilizer only with higher contents of flame retardant can be classified.

Formulation	UL-94	Dripping
PE/EVA	Not Qualify	Yes
PE/EVA-P	Not Qualify	Yes
PE/EVA/C20-6	Not Qualify	No
PE/EVA/I28-6	Not Qualify	No
PE/EVA/MH-20	Not Qualify	Yes
PE/EVA/PEgDMAE/I28-6/MH-30	V-0	No
PE/EVA/PEgDMAE/I28-6/MH-40	V-0	No
PE/EVA/PEgDMAE/C20-6/MH-30	V-0	No
PE/EVA/PEgDMAE/C20-6/MH-40	V-0	No
PE/EVA/EVAgMA/I28-6/MH-30	Not Qualify	No
PE/EVA/EVAgMA/I28-6/MH-40	Not Qualify	No
PE/EVA/EVAgMA/C20-6/MH-30	V-0	No
PE/EVA/EVAgMA/C20-6/MH-40	V-0	No

 Table 2. Properties UL-94 flame



**Figure 3.** Flame progression with dripping (a) PE/EVA/MH-20 and no dripping (b) PE/EVA/C20-6.



Figure 4. Flame test PE/EVA/PEgDMAE-13/I28-6/MH-30



PE/EVA/PEgDMAE-17/C20-6/MH-30

#### **Mechanical Properties**

Table 3 shows Tensile Strength, Modulus (MPa) and Elongation at break (%) values for the nanocomposites formulated with 30 and 40% of MH. Comparing the results of tensile strength and modulus of nanostructured systems with reference materials, an increase in these properties is observed in most of the compounds, as a result of better interaction between the polymer and Nanoclays and an increase on the content of flame retardant. While the elongation at break shows only slight decrease mainly due to less flexibility. By using PEgDMAE compatibilizer, with both flame retardant materials, a slight improvement in tensile strength was observed, due to a better interaction between amine groups and the OH groups of clay and flame retardant. While the modulus and elongation at break did not show marked differences in their values. For all evaluated properties a similar behavior for the I28 and 20A was observed. An increase in modulus and a decrease in the percentage of elongation were observed when the flame retardant was increased. While tensile strength does not show an apparent change. This is attributed to the greater rigidity of the system.

	Módulus	Tensile Strength	Elongation
Formulación	(MPa)	(Mpa)	(%)
PE/EVA	68	13.2	524
PE/EVA-P	72	11.7	245
PE/EVA/C20-6	71	12.2	529
PE/EVA/I28-6	70	10	474
PE/EVA/MH-20	73	14.7	536
PE/EVA/PEgDMAE/I28-6/MH-30	195	18	207
PE/EVA/PEgDMAE/I28-6/MH-40	260	13	195
PE/EVA/PEgDMAE/C20-6/MH-30	127	19.1	423
PE/EVA/PEgDMAE/C20-6/MH-40	195	19.2	242
PE/EVA/EVAgMA/I28-6/MH-30	159	17.5	295
PE/EVA/EVAgMA/I28-6/MH-40	184	11.6	161
PE/EVA/EVAgMA/C20-6/MH-30	195	17.1	204
PE/EVA/EVAgMA/C20-6/MH-40	239	16.9	140

Table 3. Mechanical properties of nanocomposite PE/EVA

### Conclusions

PEgDMAE promoted that the clay and magnesium hydroxide (MH) had a better degree of dispersion, through the interaction of the amine groups in the compatibilizer PEgDMAE with the OH groups of the clay and flame retardant. According to UL-94 a large number of formulations can de classified when using PEgDMAE, this was attributed to a synergistic effect between clay (carbonaceous layer generation) and MH retardant (protecting the material by releasing water during combustion). Mechanical properties showed better results for nanocomposites with PEgDMAE and 30% of MH. It was possible to reduce the amount of metal hydroxide at 30%, with satisfactory mechanical strength and flame retardancy, and could be classified as V-0. The with best balance properties were: PE/EVA/PEgDMAE/C20mixtures of 6/MH30>PE/EVA/EVAgM/C20-6/MH30>PE/EVA/PEgDMAE/I28-6/MH30.

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# PREPARATION OF NANOCOMPOSITES HDPE / EXPANDED GRAPHITE IN MIXING CHAMBER. EVALUATION OF THE FEASIBILITY OF GRAPHITE EXFOLIATION BY PHISICAL MEANS

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In the broad field of nanotechnology, nanocomposites based on polymer matrices have become an interesting area for research and development. The nanocomposites with "exfoliated" particles such as clays have been extensively studied and it has been observed that these nanoparticles give to the composite remarkable barrier properties, flammability resistance, improved mechanical properties, etc. However, there are other particles which are capable of being exfoliated such as graphite. It has generated great interest as a reinforce in polymers because of its potential to modify mechanical and electrical properties [1]. If graphite is exfoliated to obtain nanoscale films and is dispersed in a polymer matrix, this can significantly improve the properties of the compound at relatively low concentrations compared with other reinforcing carbon such as carbon black, and carbon fibers [2]. In this work, composites polymer / expanded graphite will be elaborated under conditions of high shear in a mixing chamber, trying to generate a mechanical exfoliation of graphite to obtain individual sheets of carbon called Graphene.

Composites were characterized by TGA, DSC, melt rheology, solids rheology, SEM, and a percolation curve was constructed.

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# MORPHOLOGICAL STUDY OF NATURAL RUBBER/CLAY/TIO<sub>2</sub> NANOCOMPOSITES OBTAINED BY LATEX BLENDING

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# Abstract

A series of Natural Rubber/Glicerol/Organoclay/Titanium Dioxide (NR/G/C30B/TiO<sub>2</sub>) blends were obtained via latex. The inorganic components were previously dispersed on glycerol to facilitate blending with the latex. The resulting products were studied by TGA and FTIR. The results showed significant increases in thermal stability of natural rubber above a temperature of 400 °C. This behavior occurred because to the protective effect of nanoclay and TiO<sub>2</sub> particles. Due to interactions between -OH species, a convenient compatibility of the inorganic components with glycerol and natural rubber was assumed.

# Introduction

Polymer-layered silicates nanocomposites have been widely studied due to their mechanical, thermal, gas barrier, among others properties, are greatly enhanced compared to the polymer matrix alone [1]. The improved properties are due mainly to the protection generated by nanometer-thick layers of clay when they are dispersed on the polymer [2].

Natural rubber is one of the most widely used polymers and demand worldwide due to their physicochemical characteristics. In Mexico, natural rubber is obtained from *Hevea Brasiliensis* tree. Due to weather conditions required for growing the tree, few Mexico states that grow the rubber tree. Papaloapan area, which covers a part of state of Veracruz and Oaxaca, is highly productive natural rubber. The processing of rubber in this area is through basic methodology, which generates rubber products without added value. In general, even when the viscoelastic properties of natural rubber are convenient requires additives and/or vulcanization to be highly used [3]. In recent years, several researchers have studied the formation of natural rubber nanocomposites in order to increase its mechanical strength [4] and its capacity as a barrier to gases.

On the other hand, titanium dioxide is a compound that has been used as an additive or reinforcing in thermoplastic polymers [5]. Although, photocatalytic ability can interact with acid groups or degrade organic molecules and bacteria [6,7]. The possibility of action of  $TiO_2$  may depend largely on particle size [7], whereas a smaller particle size the greater the surface area and photocatalytic action. Another important factor for the efficient application of the  $TiO_2$  is adequate support for inorganic dust.

According to the above, this paper shows the study of incorporation via latex of titanium dioxide and an organoclay on a matrix of natural rubber.

# Experimental

#### **Composites preparation**

An organoclay denoted as cloisite 30B (C30B) was used. Concentrations of 1, 3, 5, 7 and 9 wt.% titanium dioxide P-25 from Degussa were studied. Inorganic powders were first dispersed in glycerol under different time. The dispersion glycerol-C30B-TiO<sub>2</sub> was added to latex directly obtained from the rubber tree. The reaction mixture was maintained at a temperature below 10 °C with stirring above 900 rpm. The resulting mixture was coagulated in excess methanol. Plates coagulated NR/G/C30B/TiO<sub>2</sub> compounds were dried for 24 hours at room temperature for further characterization.

# Characterization

The spectra of the NR/G/C30B/TiO<sub>2</sub> composites were obtained in a Spectrum-100 infrared spectrometer of Perkin Elmer with ATR accessory. A range of 4000 to 500 cm<sup>-1</sup> and a resolution of 4 cm<sup>-1</sup> were used. The thermal data were obtained in a simultaneous thermal analyzer STA-6000 of Perkin Elmer, in an inert atmosphere of nitrogen. 10 mg of sample was used. This undergoes a non-isothermal heating, ranging from 30 to 700 °C, at a rate of 10 °C/min.

### **Results and Discussions**

The latex obtained from rubber tree contains in addition to rubber, various components that may be degraded or consumed by bacteria. The first favorable result was to prevent bacterial degradation of rubber by coagulation in methanol. Glycerol greatly facilitated the dispersion of C30B and TiO<sub>2</sub> inorganic powders. Viscosity results revealed good dispersions in glycerol as a function of time. This study allowed selecting a pre-dispersal system latex aggregation.

FTIR spectra shown in Figure 1 indicate the characteristics signals of the natural rubber. In presence of glycerol, changes between 1100 and 1030 cm<sup>-1</sup> belonging to -OH species are observed. This may indicate that glycerol remains miscible in the complex system. This behavior maintains a grade of compatibility between the rubber and glycerol and can allow also potential interactions of the glycerol with the clay and titanium dioxide. It is reported that vibrations of Ti-O-Si bond occurs at 1030 cm<sup>-1</sup> [8]. Therefore, it is possible that the interactions occur also between the inorganic components and natural rubber. There is also the evolution of a broad band below 800 cm<sup>-1</sup>, which correspond to Ti-O-Ti bond vibration. It has been reported that the presence of this band indicate interactions between TiO<sub>2</sub> and polymer matrix [8-10].

The results of thermogravimetric analysis of NR/G/C30B/TiO<sub>2</sub> composites are shown in Figure 2. The typical onset decomposition temperature of natural rubber chains at approximately 320 °C is observed. After 640 °C, some residue is not observed, because the natural rubber was obtained and processed without additives or stabilizers. Glycerol gives the rubber plasticizer character though its thermal stability is low. The degradation of glycerol molecules occurs around 200 °C. The C30B organoclay generates a protection rubber thermal degradation above 350 °C. It is known that nanozised plates can function as a shield to thermal degradation [11]. It is important to note that more residues are obtained with TiO<sub>2</sub>. We assume that particles of inorganic constituents confine to char, not allowing its conversion to carbon dioxide or volatile gases.



**Figure 1.** Spectra by FTIR of NR/G/C30B/TiO<sub>2</sub> composites. A: natural rubber, B: natural rubber/glycerol, C: NR/G/C30B, D: NR/G/C30B/TiO<sub>2</sub>-1, E: NR/G/C30B/TiO<sub>2</sub>-3, F: NR/G/C30B/TiO<sub>2</sub>-5, G: NR/G/C30B/TiO<sub>2</sub>-7, H: NR/G/C30B/TiO<sub>2</sub>-9.



Figure 2. Thermographs of NR/G/C30B/TiO<sub>2</sub> composites.

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Titanium dioxide increases protection to thermal degradation of the rubber chains mainly above 400 °C, and in relation to its content, such as reported by other authors [5,8,10] (it is shown in Figure 3). This study will be complemented with morphological analysis by SEM and XRD.



Figure 3. Weight ratio at different temperatures of NR/G/C30B/TiO<sub>2</sub> as a function of TiO<sub>2</sub>

#### Conclusions

NR/G/C30B/TiO<sub>2</sub> composites were developed via latex. The glycerol allowed homogeneous dispersion of inorganic powders and provided compatibility with latex. Coagulation in methanol allowed obtaining rubber composites without bacterial degradation. Possible interactions between the C30B and TiO<sub>2</sub> inorganic components were permitted by glycerol, which remained in the complex system. The TGA results showed significant increases in thermal stability of the composites above 400 °C, depending on the content of TiO<sub>2</sub> and the added nanoclay. Both inorganic components caused a restriction of organic residues at high temperatures.

#### Acknowledgments

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# PREPARATION AND CHARACTERIZATION OF MODIFIED STARCH/CLAY NANOCOMPOSITES FILMS

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#### Abstract

A series of modified banana starch mixtures with two clays, one natural montmorillonite and one organomodified denominated cloisite 15A (C15A) were obtained. Composites were obtained from the chemical modification of banana starch with citric acid and in situ dispersion of clay. Composites films were prepared by casting and characterized by FTIR, TGA and XRD. Good chemical modification was confirmed by the formation of ester species. The hydrophilic character of natural montmorillonite clay allowed greater interaction with the starch, resulting in the confinement of starch chains in the galleries of the clay. The thermal stability of starch was altered by chemical modification and dispersion of clay. The organic character residue was trapped by the clay plates.

### Introduction

Starch is an abundant natural polymer, contained in various agricultural products such as corn, potato and banana. The use of this compound in the preparation of new materials has attracted much attention mainly due to its ability biodegraded. However, the use of native starch has been limited mainly due to its fragility, the deterioration of mechanical properties under ambient conditions (exposure to moisture) and low processability [1]. Chemical modification of starch by esterification of polysaccharides with organic acids or acid derivatives is one of the most versatile transformations of these biopolymers [2-4]. Moreover, in recent years has been reported to obtain polymer-silicate nanocomposites with mechanical, thermal and physicochemical properties increased, using clays are dispersed on the polymer [5,6]. The precise combination of natural polymer such as starch and clay can be generated as a result a composite material reinforced and with biodegradable characteristics. Therefore, this paper shows some of the results of compounding of modified starch/clay composites.

# **Experimental**

# **Composites preparation**

Plantain starch was isolated under a process of milling, screening, washing and drying. The isolated starch was dissolved in distilled water and chemically modified with citric acid and sodium hypophosphite as a catalyst under different synthesis times (20, 30, 40, 50, 60, 70 and 80 min). During the reaction was added to a concentration of 5 wt.% one of two types of montmorillonite clay, natural clay or organically modified clay called C15A. The reaction was carried out at 80 °C and 650 rpm. Films were prepared by casting using glycerol 25 wt.% with respect to starch. The experiments shown here are only those synthesized at 50 minutes.

# Characterization

The spectra of the NS/Clay and MS/Clay composites were obtained in a Spectrum-100 infrared spectrometer of Perkin Elmer with ATR accessory. A range of 4000 to 500 cm<sup>-1</sup> and a resolution of 4 cm<sup>-1</sup> were used. The thermal data were obtained in a simultaneous thermal analyzer STA-6000 of Perkin Elmer in an inert atmosphere of nitrogen. 10 mg of sample was used. This undergoes a non-isothermal heating, ranging from 30 to 700 °C, at a rate of 10 °C/min. The diffraction patterns of the films were obtained with a X-ray diffractometer Bruker Axs, model D8 Advance, using a Cu-K alpha radiation generator with Ni filter. The tests were run in 2 theta of 1-40 ° with an intensity of 30 mA and a voltage of 40 kV.

# **Results and Discussions**

FTIR results of the starch chemical modification are shown in Figure 1. The absorption band above 1700 cm<sup>-1</sup> enclosed in a box indicates the formation of ester groups derived from the interaction of citric acid with starch –OH species. According to this result, the starch chemical modification was obtained successful. The spectra of native and modified starch/clay composites (NS/MMT, MS/MMT or MS/MMT, MS/C15A) are shown in Figure 2. A slight decrease in overtone around 1740 cm<sup>-1</sup> is observed in the mixture of native starch with natural montmorillonite. Possible impediments to bond vibrational motion esters species, due to the confinement of some starch chains in the galleries of the clay are occurring.



Figure 1. Spectra by FTIR of native and modified starch

The chemical modification also affected the thermal behavior of starch, as is shown in Figure 3. At low temperatures there is a higher thermal stability for modified starch than native starch. However, the chemical modification causes a decrease in onset temperature of degradation of the starch chains, observed at about 285 °C. Although the higher the temperature, the residue is much higher with the chemical modification. This behavior indicates that the chemical modification may cause the formation of weak structures and easy to degrade. Although higher temperatures can be

forming crosslinked structures difficult to degrade. The natural montmorillonite clay has more influence in changing thermal behavior than the C15A clay, as shown in Figure 4. The hydrophilic character of natural montmorillonite can cause a higher compatibility with the starch, which also is hydrophilic [7].



Figure 2. Spectra by FTIR of native or modified starch/clay composites



Figure 3. Thermographs by STA of native and modified starch

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Figure 4. Thermographs by STA of native or modified starch/clay composites

X-ray diffraction patterns shown in Figure 5 reveal differences in the crystalline region of starch. Another crystalline form may be occurring as a result of interactions during the chemical modification, changing the type-A pattern to type-B pattern. The clay promotes a low-angle crystalline character observed in Figure 6, as an effect of intercalation of polymer chains in the galleries of the clay [8].



Figure 5. Patterns by X-ray diffraction of native and modified starch

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Figure 6. Patterns by X-ray diffraction of native or modified starch/clay composites

### Conclusions

Starch composites with clay were obtained, through chemical modification of starch with citric acid and dispersion of clay in situ. The results of the absorption bands related to the formation of esters gave evidence of chemical interactions of citric acid with the starch –OH species. Chemical modification affected the thermal stability and crystalline type of starch. Intercalated morphology was observed by the increase in interlayer spacing of the natural montmorillonite clay, indicating the possible confinement of starch chains inside the galleries of clay due to the hydrophilic compatibility of the clay with starch.

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# PET-PEN NANOCOMPOSITES

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Nanocomposites materials from thermoplastic polymer and clays are being developed mostly by their physicochemical characteristics. The key to produce these materials basically consists of three steps, the compatibility of nanoparticles with polymer matrix, exfoliation of clay tactoids and the distribution and dispersion within the polymer. This paper presents the results of blends made of PET, PEN and clay bentonite modified with L-Lysine amino acid. For exfoliation and distribution of nanoparticles in polymer matrix was used a mixed- static head coupled to a single screw extruder designed to generate extensional flows. The mixtures were characterized by TGA, DSC, SEM, NMR, oxygen permeability and parallel plates rheometry. Regarding pristine PET properties, results pointed of that Tg of the blends was improved up to 15°C, tensile mechanical properties like elastic modulus, strain and stress were no affected and fracture strain decreased largely, oxygen permeability decreased significantly and shear viscosity showed shear thinning behavior. Optimum results were obtained when PET-PEN transesterification reaction generated a block-random structure mainly. Films and packaging for foodstuffs and beverages which have to be subjected to pasteurization process could be produced with these nanocomposites.

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# STRESS RELAXATION EFFECT ON THE ELECTRICAL RESPONSE OF EXPANDED GRAPHITE/SEBS NANOCOMPOSITES

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Graphene nanosheets and Graphite filled poly(styrene–ethylene/butylene–styrene) (SEBS) composites with different concentrations were studied, observing their electrical, mechanical and stress relaxation properties. The composites were prepared by melt compounding. Graphene nanocomposites present higher electrical conductivity and a lower percolation threshold than Graphite composites. The stress relaxation results show a decrement of composite electrical resistance with the increase of time when a condition of deformation outside the linear viscoelastic region was applied.

# PREPARATION OF COMPOSITES FROM CHICKEN FEATHERS AND PVC

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# Abstract

A composite from PVC-chicken feathers (CF) was prepared by means extrusion in several CF concentrations, using semi-rigid PVC composite from profiles applications. Effect of CF over physicochemical properties was evaluated by means thermogravimetric analysis (TGA), Dynamic mechanical analysis (DMA) and mechanical properties were evaluated. A frequency sweep in DMA was carried out to evaluate possibility to determinate sound isolation applications on PVC-CF composites. Effect of frequency over storage modulus and tan delta curves was evaluated. Thermal stability of composites was lower than PVC pure, being composite with 10 % CF the lowest. Also differential scanning calorimetry (DSC) was carried out to evaluate glass transition temperature.

# Introduction

The development of new composite materials from natural sources is a research area in continuous growth. Nowadays, there exist different unexplored sources which could contribute to environmental applications. Research focus to find the best combination of synthetic and natural resources to allow obtain new materials with improved properties in comparison to the characteristics of the constituents by themselves. Chicken feather (CF), a world waste without any relevant application, is a natural source of keratin which has good mechanical and thermal properties; taking advantage of this fact, some feathers components have been used as reinforcement of synthetic polymer in the development of new composite materials[1, 2].

The use of natural fibres in plastic matrix brings new options about improvement of mechanical and physicochemical properties. So natural fibres reinforced plastic composites have achieved applications in decking, furniture components, door moldings, packing pallets and interior panels of automobiles [3]. However, there is poor interfacial adhesion between the hydrophobic matrix and the hydrophilic fibre. If no modification of fiber or compatibilization of the two materials is developed, the weak interfacial adhesion between fiber and matrix usually results in poor mechanical properties of the composites [3].

CF was use to prepare composites with Polyolefins, CF-Polypropylene (PP) composite was prepare obtaining a material that showed better compatibility and acoustic properties compared with jute and other natural fibers [4]. Also CF-High density Polyethylene (HDPE) composites have been prepared, founding that CF provides s stiffness increase of HDPE, furthermore a better thermal stability over 200°C [5, 6]. Poly (methyl methacrylate) (PMMA) is other polymer used to prepare composites with CF, showing better thermal properties than PMMA [7].

There are several reports of CF composites, but just a few with Poly (vinyl chloride) (PVC). A PVC-baggase fiber was prepared and use of a benzoic acid as compatibilizer showed effective

adhesion promotion to obtain a good compatibilization of baggase and PVC [3].

Poly vinyl chloride (PVC) is thermoplastic polymer with a wide range of applications, being construction profiles one of most important. Rigid PVC composite show good environmental properties, impact and temperature resistance.

In this research work preparation of PVC-CF composite was prepared by extrusion in different ratios (5, 10 and 15%). Thermal properties were evaluated by means dynamical mechanical analysis (DMA) and thermogravimetric analysis (TGA).

# Experimental

# **Composites preparation**

CF consists of barbs and barbules and quill, the central materials of feathers. In this work quill was the materials used to prepare composites. Quill was obtain from feathers by manual procedure, feathers were cutted from chicken feathers and after quill was cutted in small pieces. PVC and quill were mixed in a bag.

CF-PVC composites were prepared by means extrusion in a Beautelspacher mono screw extruder; with a temperature profile of 185, 200 and 215 °C. Composites with 5, 10 and 15% of CF content were prepared.

# **Composites characterization**

DMA studies were evaluated in TA instruments equipment model 2980, a single frequency mode and dual cantilever clamp were used. Analysis conditions were 1 Hz frequency, and a temperature sweep from 30 to 180°C with a 5°C/min ramp. Also a frequency sweep from 1 to 100 Hz was carried out to evaluate frequency effect over storage modulus and tan delta curves.

TGA studies were carried out in a TA instruments equipment model Q5000. Conditions were a temperature ramp of 10°C/min, from 30 to 600°C using 20 mg of sample, under nitrogen atmosphere.



Figure 1. Storage modulus (left) and Tan delta (right) curves of PVC and PVC-CF composites obtained in DMA.

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# **Results and Discussion**

Figure 1 shows storage modulus curves of PVC and PVC-CF composites with different CF content. It observe that under 90°C only PVC-CF 5% composite have a storage modulus higher than PVC pure, but over 100°C 3 composites show a higher modulus value. This is indicative that CF addition in PVC causes an improvement in viscoelastic properties in high temperatures, which can be associated to keratin increase the capability to energy transfer in interface. In the other hand, tan delta curves show there is not a considerable effect of CF inclusion in PVC over transitions, due all materials present a peak around 97°C associated with glass transition of PVC. However, there is a significant effect over damping, which decreases with CF content except for CF 5%. The damping diminishes due polymer chains added to keratin decrease its mobility, decreasing reducing friction between them.

Figure 2 shows the effect of frequency over storage modulus for PVC, it can observe that with frequency values from 1 to 60 Hz storage modulus increase but with higher frequencies decrease, being lower than frequency of 1 Hz. Compare with PVC-CF 10% composite a similar behavior is observed, but with high frequency values the storage modulus is similar than low frequency values. This behavior can be explain in function of periods of time within materials are submitted at low stress, that means polymeric chains have no relaxation times long enough to recover or reorder presenting a rigid behavior.



Figure 2. Effects of frequency over storage modulus obtain by means DMA for PVC (left) and PVC-CF 10% (right).

TGA curves (figure 3) shows PVC decomposition in 2 main steps, first one around 240°C due dechlorinization (lost of HCl) of PVC and formation of double conjugated bonds, and a second step around 420°C due breaking of first step polymeric products [8]. Comparison of TGA curves of PVC with PVC-CF composites show a similar decomposition steps compared with PVC pure, but a lower thermal stability, being PVC-CF10% the lower temperature of decomposition. Keratin, the main component of CF decomposes between 216 and 410°C, range where destruction of disulfur bonds and H2S elimination take place. This process corresponds to denaturalization of b structure, followed by thermal pyrolisis of main chain bonds, peptidic bonds, and degradation of backbone. In this region occur diverse chemical reactions where proteinic compounds decompose in lighter and volatile compounds like H2S, CO2, H2O and HCN.



Figure 3. TGA curves for PVC (left) and PVC-CF composites (right).

### Conclusions

It was possible obtain composites from PVC and CF in different CF amount by means extrusion without compatibilizer. In this research work 5, 10 and 15% were evaluated, and thermal characterization by means DMA and TGA show differences between PVC pure and PVC-CF composites. Storage modulus obtaind by means DMA show that in low temperature only PVC-CF 5% has a higher modulus value but over 100°C all composites have a higher modulus value compared with PVC pure. Frequency sweep study shows that PVC storage modulus decreases with high frequency values, for PVC-CF composites storage modulus increases with frequency, being the PVC-CF 10% composite with higher values.

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# FORMATION OF NANOHYBRID SHISH KEBABS IN POLYETHYLENE NANOCOMPOSITES USING FUNCTIONALIZED CARBON NANOTUBES

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### Abstract

It is known that the functionalization of carbon nanotubes (CNTs) modifies their application due to the affinity with distinct materials such as cement, polymers, etc. In the present work, the functionalization of single walled carbon nanotubes (SWNTs) with the p-aminobenzenesulfonamide was carried out to increase their solubility in different organic solvents and better affinity with of polymer matrices. The functionalized SWNTs were characterized by SEM and TEM. The polyethylene nanocomposites were prepared using functionalized SWNTs and processed by the method of solution blending. Characterization of polyethylene nanocomposites by SEM shows the formation of shish-kebabs structures called elsewhere as nanohybrids shish-kebabs (NHSKs), where the carbon nanotube is the shish and the crystal of polyethylene is the kebab.

# Introduction

CNTs exhibit excellent mechanical and electrical properties, low density and high surface, this properties make ideal candidate for reinforcement of nanocomposites with polymers [1-3].

In general, a series of polymer nanocomposites with addition of CNTs have been studied. In many cases, the contribution of the CNTs inproves the mechanical properties of polymers matrices and, as a result, offers their applications in automotive, space, and other fields.

However, the agglomerations of carbon nanotubes make difficult the dispersion and interaction with the polymeric matrix. The functionalization of CNTs has been employed by introduction of molecules and modification of their surface chemistry, by covalent and no-covalent methods with the final enhancement of solubility of the CNTs, resulting better interaction with the matrices as polymer, cement, metals, etc. [4,5]. As a result of the present work, we functionalized SWNTs with p-aminobenzenesulfanoamide for preparation of nanocomposites with polyethylene by solution crystallization.

# Experimental

# Functionalization of carbon nanotubes.

SWNTs was purchased for Nanostructured & Amorphous Materials Inc. Urea, paminobenzenesulfonamide, and xylene were purchased from Aldrich. High density polyethylene Mw 200,000 g/mol was purchased from Aldrich. The functionalization of SWNTs was realized using Schlenk technique in atmosphere of nitrogen (Fig.1) [6].



Figure 1. Scheme of the functionalization of SWNTs.

#### **Preparation of nanocomposites**

The preparation of nanocomposites of polyethylene was carried out according to the technique reported by Li et al. [9]. The morphology and structures of nanocomposites and SWNTs functionalized were studied by scanning electron microscope (SEM) and transmission electron microscope (TEM).

#### **Results and Discussion**

The functionalization of the SWNTs with aryldiazonium salts in molten urea represents a useful method for covalent functionalization (Figure 1). The functionalized SWNTs with aminobenzenesulfonamide were purified and analyzed by transmission electron microscope (TEM), the micrography show the covalent bonding between the SWNTs and organic molecules over the nanotubes (Figure 2). This figure, obtained by TEM, shows that the carbon nanotube has organic molecules in its surface corresponding to benzenesulfonamide, attached covalently. It is necessary to mention that the ring formation, called "cut of onions", results that this morphology of CNTs has important magnetic properties, needed to study in further research.



Figure 2. TEM image SWNTs-benzenesulfonamide

The covalent functionalization of SWNTs in molten urea represents an exellent method for obtaining promising materials, for example nanocomposites with different polymers as polyethylene because of their better capacity to form mixed polymer matrices.

In respect with the results on polyethylene nanocomposites with the SWNTs, as it was analyzed by SEM, the image in the figure 3 shows the formation the shish-kebab morphology, which was reported as nanohybrid shish-kebabs (NHSKs) structure in the literature; the nanotube is the shish, and the crystal of polyethylene is the kebab [7,8]. These structures have relation with classic shish-kebab ones [10]. In this structure, the central shish corresponds to the functionalized carbon nanotubes acting as a nucleating agent, whereas the polymers chains start to fold forming the kebabs (they are formed by polyethylene crystal).

Crystallization temperature is an important factor for the formations of NHSK; thus, in this research, the solution temperature was controlled at 103°C for one hour.



Figure 3. A) Nanohybrid shish-kebabs of functionalized nanocomposites polyethylene-SWNTs; B) Representation of structure of the nanohybrid shish-kebabs.

In this system, the achievement of the formation of the shish-kebab with a periodicity of 33.5 nm and average thickness of 26.66 nm was observed. This value is in average in 10-15 nm bigger than reported by Li et col. [9]; that maybe is possible due to the fact that the carbon nanotubes form with organic molecules the folds of lamellar crystal of polyethylene over carbon nanotubes surfaces, thus increasing the crystal size. The polymer (kebab) periodically grew perpendicularly to the SWNTs. It could be related with the fact that first a coating with the polymer takes place and then it begins to nucleate the coated polymer on the carbon nanotube forming the kebab.

In summary, the preparation the nanocomposites of polyethylene with carbon nanotubes functionalized by urea as a solvent and organic molecules of aryldiazonium, results a major dispersion in the polymeric matrix, forming nanocomposites a shish-kebab nanohybid. It is necessary to mention, that the mechanical and electrical properties (in particular conductivities) of these materials might be further improved.

#### Conclusions

The functionalization of SWNTs with p-aminobenzenesulfonamide allows major dispersion and interaction with polyethylene matrix. The preparation of the polyethylene nanocomposites with functionalized SWNTs by crystallization-controled solution method can result nanohybrid shish-kebab structures.

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# BLENDS OF DENDRONIZED POLYMERIC NANOCOMPOSITES WITH SMALL MOLECULES AND DRUGS

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Dendronized polymers are a family of linear polymers containing complex substituents which interact specifically with small molecules[1]. The synthesis and characterization of dendronized polymers containing interacting functional groups allow to obtain complex structures by interaction with small molecules, specifically with drugs. The synthesis, characterization of monomers and polymers containing diethylaminoethylmethacrylamides and blending with different small molecules like glycine and cyclohexanediol and with drugs like ibuprofeno, paracetamol and dichlorphenaco reported.



Thermogravimetric analysis of the polymers show a two stage degradation profile and the thermal stability of PDEAEMA is lower than P2,2' DAEAEMA. Tg value for P2,2' DAEAEMA is higher than that of PDEAEMA. Blends containing both polymers and Ibuprofeno, dichlorophenaco, paracetamol, glycine and cyclohexanediol show only one Tg in the whole range of composition what indicate a compatibilization of the small molecules with the dendronized polymer. The thermal degradation of the blends show that a deliver of the small molecule take place at differte temperatures depending on the composition.

FT-IR spectra show several displacements of the signals as the composition of the blend increases. The synthesis and characterization of polymers containing different amino centers, allow to obtain the first generation of dendronized polymers which interact, with small molecules and drugs.

Finally, we present certain selected cell-biological results that pertain primarily to applications in orthopaedic and vascular medicine, and we discuss the influence of surface properties on the observed behavior of various relevant cell lines.

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# SYNTHESIS AND CHARACTERIZATION OF THERMOSENSITIVE CORE-SHELL NANOPARTICLES

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Research on the synthesis and characterization of thermosensitive polymeric particles has received increasing attention in the last years, because of their unique properties [1,2]. Thermosensitive coreshell polymeric particles usually consist of a core of polystyrene (PS) and a shell of a polymer of acrylamide derivatives [2]. In a water dispersion at temperatures below the lower critical solution temperature (LCST), water swells the thermosensitive shell. At temperatures higher than LCST the shell shrinks, releasing water molecules and leading to a decrease in the particle size. Despite their potential applications, a detailed search in the specialized literature showed a total absence of reports about the preparation of thermosensitive core-shell polymeric nanoparticles. The synthesis of very small thermosensitive core-shell polymeric particles can be achieved starting with the preparation of the core by semicontinuous heterophase polymerization. Similar to batch microemulsion polymerization, this technique is capable of producing polymeric nanoparticles of 20-50 nm in average diameter [3,4].

Thermosensitive core-shell nanoparticles were synthesized by semicontinuous heterophase polymerization of styrene, followed by a seeded polymerization for forming a shell of poly(N-isopropyl acrylamide). Nanoparticles characterization by scanning transmission electronic microscopy showed core-shell morphology with average particle diameters around 40 nm. An inverse dependence of the particle size with temperature in the range 20-55 °C was identified by quasielastic light scattering measurements. As was expected for core-shell particles with PNIPAM as the shell, a volume phase transition near 32 °C was detected. In spite of thermosensitive properties of core-shell nanoparticles synthesized here, the volume % loss values were not so high, probably due to their relatively low content of PNIPAM.

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# DEVELOPMENT AND EVALUATION OF ELECTROCHEMISTRY DISPERSIONS OF CARBON NANOTUBES AS AN AGENT DISPERSIN USING POLYMETHYLMETHACRYLATE

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#### Abstract

The use of polymers as dispersants for carbon nanotubes (NTC) is one of the strategies employed in recent years [1-3], this in order to transfer the properties of the NTC to polymeric materials by preparing composites [4] between the properties of the NTC are very good electrical conductivity, a property that can be leveraged to transform materials into conductors insulators [5, 6], modulating these behaviors through the concentration of NTC.

This work shows that the use of PMMA synthesized by ex-situ photocatalysis has proved to be a good dispersant for carbon nanotubes, this in a chloroform solution, indeed, the use of such dispersions allow to form conductive films showing electrochemical activity redox couple in front of the Fe3 + / Fe2 + and hydrogen peroxide.

#### Introduction

The use of polymers as dispersants for carbon nanotubes (NTC) is one of the strategies employed in recent years [1-4], this in order to transfer the properties of polymeric materials to NTC through the preparation of composite materials between the properties of the NTC are a very good electrical conductivity, a property that can be leveraged to transform materials into conductors insulators, modulating these behaviors through the concentration of NTC

Once you are made of composite materials with good electrical conductivity, one of the applications that have been given is the manufacture of electrodes, this in order to detect and quantify chemical species in solution such as cholesterol [5] nucleic acids [6], proteins [7, 8], dyes [9, 10] or clenbuterol [11], among others. The polymer selected to carry out the dispersion of carbon nanotubes is a function of dispersant capacity, but not only that, it is also directly related to the desired analyte quantification, therefore, each NTC dispersion prepared with different polymers can observe a different response, in the case of uric acid and ascorbic acid have been used polymers such as polystyrene sulfate [12], polyacrylic acid [13] or Nafion ® [14] to name a few

The polymethylmethacrylate (PMMA) has been used to prepare dispersions of NTC [15, 16] but has not so far shown the use of these dispersions in electrochemical applications. The work done in our work group has shown that the use of PMMA synthesized by photocatalysis ex-situ has proven to be a good dispersing agent NTC in solution and that these nanocomposites showed electrochemical activity versus redox couple Fe3 + / Fe2 + and analytes such as ascorbic acid and uric acid, which allows us to suggest its use in the manufacture of electrochemical sensors

# Experimental

# Synthesis of polymethylmethacrylate

In a glass tube was added (10g) of MMA, the photoinitiator with conc. 1x10-3 M. Then placed in the reaction system. Bubbled with N2 for 5 min. before the start of irradiation and continued bubbling for 60 min. We used tungsten-halogen lamp of 100 watts. After the reaction was added excess methanol to precipitate the polymer formed.

# Preparation of the dispersions of NTC-PMMA

A solution of PMMA at a concentration of 1 mg / mL in chloroform, this solution was used for preparing dispersions at concentrations of 1 NTC NTC mg per mL of the solution of the polymer, so that these dispersions were homogeneous ultrasonic bath was used in which dispersions were immersed for 10 min

# Modification of glassy carbon electrodes

The dispersions prepared were used for the formation of a film on the surface of glassy carbon electrodes by evaporation of the solvent, glassy carbon electrodes were previously polished with alumina suspensions of 1.0, 0.3 and 0.05 microns, rinsed with deionized water and dried under a stream of  $N_2$ .

# **Electrochemical measurements**

All electrochemical measurements were carried out in phosphate buffer pH 7.4 using a model BAS Epsilon potensiostato and a three-electrode electrochemical cell using a platinum wire counter electrode, reference electrode of Ag / AgCl as working electrode used a glassy carbon electrode modified with NTC-PMMA dispersions which will henceforth be called CV / NTC-PMMA

### **Results and Discussion**

Figure 1 shows the cyclic voltammograms of 1 mM potassium ferricyanide in phosphate buffer, clearly showing the process of oxidation of Fe 3 + at a potential of -76 mV and a current of 11.59 uA, the oxidation process a potential of 178 mV and a current of 9.92 uA, this results in an Ep of 254 mV  $\Delta$  and a peak current ratio of 0.85, this indicates that the charge transfer process is complicated with respect to a carbon electrode bare glassy, however as we know the use of NTC can help separate the signals from a mixture of analytes as discussed below



Figure 1 Cyclic Voltammetry of 1 mM potassium ferricyanide in phosphate buffer pH 7.4 electrode using CV / NTC-PMMA, v = 100 mV / s.
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In figure 2 shows the batch chronoamperometry using the steady-state electrode CV / NTC-PMMA at a potential of -200 mV which is the potential which is observed in the cyclic voltammograms Fe3 + was completely oxidized and is most suitable for maximum power development. It is noted that the current response to each addition of potassium ferricyanide solution at concentrations ranging from 10 to 90 nM is immediate and proportional, the latter is most clearly seen in the insert which shows the calibration curve which indicates the electrode used to have a sensitivity of 9.8 mA / mM and a linear fit of 0.99979.



Figure 2 Cronoamperograma batch using a steady-state CV electrode / CNT-PMMA at a potential of -200 mV and with additions of Fe (CN) 63 - 10 nM each time.

The results obtained from the experiments described are such that the electrode can be used perfectly in the quantification of electroactive species, this due to the linear current response function of the concentration of the analyte, in this case potassium ferricyanide

To show that the quantification of analytes of interest is possible, then displays the cyclic voltammetry of ascorbic acid (AA) and uric acid (UA), Figure 3 shows in the dotted line voltammograms of AA and he looks a broad oxidation process with a maximum current to 688 mV and in the case of uric acid observed an oxidation process is also very broad at 517 mV, the fact that both oxidation processes are comprehensive quantification prevents independently of each other this happens just as you are used glassy carbon electrode without modification, which would allow quantification of AU AA independently of the reduction process is observed -150 mV.



Figure 3 Cyclic Voltammetry AA (dotted line) and AU (solid line) on an electrode CV / CNT-PMMA in phosphate buffer pH 7.4, v = 100 mV / s

### Conclusions

The results presented show that the NTC-PMMA nanocomposite is as good a conductor of electricity it can use it in the manufacture of electrodes and used in the quantification of electroactive species in aqueous media. The signals from each of the two analytes of biological interest that indicate that there were signs of redox processes that can be used to quantify independently of one another. The hydrophobic nature of the nanocomposite can also achieve an electrochemical sensor is much more robust than those made of polymeric materials to the NTC who combine with water

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# METHYL METACRYLATE-CO-BUTYL ACRYLATE/CARBON NANOTUBES FILMS: EFFECT OF BUTYL ACRYLATE CONCENTRATION ON THE DISPERSION OF CARBON NANOTUBES AND THE ELECTRIC RESISTANCE SURFACE IN THE FINAL NANOCOMPOSITE

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### Abstract

Copolymers from methyl\_metacrylate-co-butyl\_acrylate (MMA-co-BuA) were synthesized by reversible iodine transfer polymerization (RITP) in toluene at 90°C, using azobisisobutironitrile (AIBN) as a free radical initiator and molecular iodine (I2) as a precursor of transfer agents [1]. The ratios of MMA:BuA were 90:10, 80:20 and 70:30 in wt-%. The monomer conversion was followed by <sup>1</sup>H NMR. The molecular weight distribution was calculated by size exclusion chromatography (SEC). Using ultrasound energy (40 kHz for 4 min) different solutions were prepared. The CNT dispersion in each solution was verified visually initially and after 72 hours of its preparation. Then nanostructured films were prepared by casting and the drying rate (N) was followed gravimetrically. Using an ACL 390 surface resistance meter, the surface film resistance in Ohms ( $\Omega$ ) was measured. The inhibition period at the beginning of the polymerization increases as a function of MMA/I<sub>2</sub> ratio. The CNT dispersion is better at high MMA concentration. A percolation threshold at 0.6-0.8 wt-% of CNT, independently of the concentration of polybutyl acrylate, was observed. The nanotubes/copolymer films had a great electric conductivity and can be used as an electrostatic discharges dissipative coating (ESD) on different items as a woven and non woven textiles.

### Introduction

Carbon nanotubes (CNT) were synthesized at first time by Iijima [1] in the 90's. They presented a cylindrical structure and they can be single wall carbon nanotubes (SWCNT) or multiple wall carbon nanotubes (MWCNT). The average diameter oscillates from 1 to 50 nm. The incorporation of CNT in polymeric and/or ceramic materials can results in an increase on some properties according to the origin materials. Properties as tensile strength, surface electric conductivity and heat transfer can be increased. A 0.5-2 wt-% of CNT concentration allows the electric conductivity in several polymers [2,3]. However, the modulus of materials increase as a function of the CNT concentration, as a consequence of its rigid structure. It could be a problem in applications where flexibility and comfort are needed, such as a coating on textile fibers in woven or non-woven fabrics. Another important factor to consider, is the nature and the structure of the polymer matrix, to obtain a polymer nanocomposite with desirable properties. The choice of the polymerization method to obtain polymers or copolymers is very important also. Typical anionic polymerization can be used to obtain block copolymers with perfect blocks. Living radical polymerization techniques had been studied [4] to obtain copolymers also. Nitroxide mediated polymerization (NMP), atom transfer radical polymerization (ATRP), reversible addition-fragmentation transfer (RAFT) and more recently reverse iodine transfer polymerization (RITP). All of them base its mechanism in the activation-deactivation of chains by specific species. These techniques establish a dynamic equilibrium between active and dormant chains, which makes the average molecular weight to be a function of the ratio of the reactants and the conversion [5].

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The RITP mechanism consists of three steps, at the beginning the initiator is dissociated in presence of monomer and molecular iodine; they react and form a transfer iodine agent with a few or without monomer units. Then, the degenerative transfer process takes place activating and deactivating the growing chains. The reaction is stopped when monomer is finished and no more transfer occurs. (see Fig. 1).



Figure 1. Schematic illustration of the steps of the RITP mechanism

Using the information described above this work was focused in the study of the effect of butyl acrylate (BuA) concentration on the dispersion and the electric properties of nanocomposites of copolymer butyl acrylate/methyl methacrylate and carbon nanotubes, where the copolymers were synthesized by RITP method.

### **Experimental**

#### Synthesis of copolymers and characterization

Block copolymers of methyl methacrylate/butyl acrylate were synthesized using butyl acrylate (BuA) and methyl methacrylate (MMA) as co-monomers and AIBN and molecular iodine (I<sub>2</sub>) as the free radical initiator and precursor of transfer agent, respectively. Different concentration ratios of the MMA:BuA were used, 90:10, 70:30 and 50:50. The co-monomers were added sequentially. Firstly, the MMA was polymerized and characterized by size exclusion chromatography (SEC) and nuclear magnetic resonance (1H NMR). Then the BuA and AIBN were added to continue with the polymerization. The final copolymer was evaluated by SEC and 1H NMR to determine the molecular weight distribution and the real composition. Differential scanning calorimetry (DSC) of the copolymers was carried out.

#### **Films preparation and Characterization**

Using the copolymers previously synthesized and MWCNT COOH functionalized at 0.4, 0.6, 0.8 and 1 wt-%, colloidal suspensions, in 10 ml of chloroform, were prepared by means of ultrasound power (40 kHz for 40 min). The colloidal suspensions were deposited on the glass sheets and the drying rate (N) was evaluated by means of the equation 1 [6]. Finally, the surface electric resistance and the percolation threshold of the films were measured using an ACL 390 surface resistance meter.

$$N = \frac{Ls}{A} \left( \frac{dw}{dt} \right) \qquad \text{eq. (1)}$$

Where, N, is the drying rate; Ls, is the dried mass; A, is the evaporation area and dw/dt, is the loss mass as a function of time [6].

## **Results and Discussions**

## Synthesis of copolymers and characterization

The product at the first step of the polymerization (MMA synthesis) was analyzed by 1H NMR, the relation of the -C=O-O-<u>CH3</u> bands at 3,6 ppm for the PMMA produced and 3.8 ppm for the MMA, were evaluated to obtain the MMA conversion. The conversions were from 0.90 to 0.92 for all of the recipes. The molecular weight distribution (polydispersity, I) reaches values from 1.5, it is a typical I for RITP method. In this same step, the MMA-I molecular weight reaches 24,000, 29,000 and 40,000 g/mol due to the MMA concentration for the final cooplymers at 50:50, 70:30 and 90:10 respectively (see Table 1). With respect at the final composition (by 1H NMR) of MMA:BuA in the cooplymers were 93:7, 80:20 and 70:30 for the corresponding recipes at 90:10, 70:30 and 50:50, respectively. The molecular weight of the second block (BuA) diminished as a function of the increase of BuA, which indicates certain selectivity of the iodine agent transfer to react with MMA or BuA to form the cooplymers in the second polymerization step. With respect to the Mn it increases from the MMA determined in all of the cooplymers synthesized, it corroborates the formation of a second block rich in BuA.

 Table 1. Vitreous transition temperature and Mn SEC evaluated for copolymers synthesized by free radical polymerization (FRP) and by RITP.

Monomer ratio		FRP	FRP		RITP		
	1H NMR	Tg(°C)	Mn (g/mol)	Tg (°C)	Mn (MMA)	Mn (MMA:BuA)	
90:10	93:7	75	69,000	9	00 44000	48000	
70:30	80:20	62	71,600	2 9	9 29000	38000	
50:50	70:30	32	83,400	-2 1	02 24000	31000	

FRP, Free radical polymerization; RITP, Reversible Iodine Transfer polymerization; Mn, average molecular weight by number.

In Table 1 is shown the DSC analysis for copolymers by free radical polymerization (FRP) and RITP. Tg at 32, 62 and 75°C were observed for the FRP copolymers, it is a typical behavior of this copolymer type, an increase in the rubber fraction provokes a decrease in the Tg. Meanwhile, for the copolymers synthesized by RITP two transitions were observed, one of them at 100 °C (PMMA block) and the other near to 0°C (PBuA rich block but contaminated with a little amount of MMA). The PBuA homopolymer Tg is near to  $-40^{\circ}$ C and the Tg was shifted in all the copolymers, due to the random composition of the BuA block (PMMA:PBuA). In Figure 1 is shown the morphology of the copolymers, where the dark part corresponds at the PBuA block (RuO<sub>4</sub>, stained) and the continuous phase corresponds to the PMMA block. The morphology did not present a defined structure (as a dots or lamellar configuration), independently of the BuA block fraction, only, an increase in the volume fraction of BuA phase in function of the BuA concentration was observed.



Figure 2. Morphologies by TEM for the copolymers a) 70:30 and b) 80:20 (scale bar at 5 nm).

#### **Films preparation and Characterization**

Visual difference of CNT dispersion in the copolymers solution was not observed, thus, we conclude, partially, that composition of BuA has not influence on dispersion of CNT. A dry kinetic to evaluate N was carried out to determine the physical interaction between the copolymers, the CNT and the solvent. It was observed a higher N in the copolymer with 30 wt-% of BuA (see Figure 3). This behavior is attributed to the strong interaction between the chloroform and the MMA block and then a lower N for the copolymer with 20 wt-% of BuA. A diminish of N was observed as a function of CNT amount. It is more significant for the copolymer 70:30 and just slightly for the copolymer 80:20. It was due to the interaction of the solvent with the MMA block and with the CNT because of COOH functionality that causes a slower evaporation (see Figure 3). For high concentration of CNT in copolymer 70:30 N decreased drastically, this behavior explained, probably, by the strong interaction of CNT by self promoting agglomerations and a poor interaction with solvent. In the evaluation of electric properties it was observed that copolymers 80:20 and 70:30 constituted with CNT the percolation threshold occurs in a CNT concentration interval of 0.6-0.8 wt-% reaching resistivity values of  $1 \times 10^8 \Omega$ . These results indicate that best dispersion of CNT is achieved under these amounts of CNT.



Figure 3. Dry rate of the copolymers as a function of CNT content.

In the Figure 4 is shown an image by SEM of the MMA-co-BuA/CNT with 20 wt-% of BuA. It is observed an excellent dispersion of CNT in the MMA-co-BuA matrix.



Figure 4. Nanostructure morphology of copolymer MMA:PBuA 80:20 at 0.8 wt-% of CNT.

# Conclusions

MMA-co-BuA copolymers were synthesized by RITP and they were used as a matrix for CNT. The nanostructure composites present a lower surface electric resistance and it would be used as an electrostatic dissipative discharges coating.

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# TECD NANOPARTICLES EMBEDDED IN POLYPYRROLE-IODINE THIN LAYERS SYNTHESIZED BY PLASMA

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### Abstract

A recent approach to the fabrication of electroluminescent devices has emerged from the development of colloidal semiconductor nanocrystalline quantum dots, called also nanocrystals or nanoparticles. Semiconductor nanocrystals are inorganic nanoparticles that can be synthesized in organic solvents or water. Nanocrystals are surrounded by an organic capping layer, and their optical and electronic properties are determined by the quantum confinement effect. CdTe nanoparticles were prepared in a solution of CdCl<sub>2</sub> and Thioglycolic acid, TGA, at room temperature with constant molar ratio Cd/TGA of 1:6 and the pH value was adjusted to 5 using a 3M NaOH solution. The mixture was heated at 92°C under open-air conditions and the luminescence began to appear, due to confinement effects, a slightly green luminescence can be observed under illumination with a 366 nm wavelength. With larger growth time, the luminescence becomes more intense, and shifted to red due to the growth of nanocrystals. Multilayer thin films were fabricated, by plasma polymerization deposit of polypirrole with Iodine (PPy/I) thin films over a glass substrate, the substrate was removed from the reactor and drops of nanoparticles solution were deposit and dried, then again to the plasma reactor to deposit the second layer of PPy/I. The process was repeated giving substrates with 1, to 5 layers of PPy/I with CdTe nanoparticles embedded in the polymer matrix. The composite characterization was done with ATR-FT-IR, SEM, X-ray and optical characterization by absorbance and photoluminescence, using a Shimadzu 2401 UV-Vis spectrophotometer and Lightspeed Technologies SPM-002-D spectrometer.

### Introduction.

The polyacetylene synthesis in 1977 by H. Shirakawa, A. G. MacDiarmid and A. J. Heeger, marks the beginning of conductive organic polymers such as polyaniline, polythiophene and polypyrrole, PPy [1-3]. The combination of electrical conductivity and the excellent polymers properties, such as mechanical strength, flexibility, stability, low cost and ease of processing has generated interest as replacements for some metals. The properties associated with semiconducting polymers are of increasing interest in applications such as batteries, sensors, electrochromic displays, electromagnetic shielding, fuel cells, light emitting devices, and biomedical devices [4]. Of the known conducting polymers, polypyrrole (PPy) has a special interest due to the long-term thermal stability and high electrical conductivity. The preparation is

easy using the electrochemical method or plasma polymerization [5]. Polypyrrole can be conductor by means of pyrolysis, doping with iodine, and incorporation of metal clusters in the polymer matrix.

The incorporation of nanoparticles in polymer matrices such as polypyrrole, is of current interest for many purposes. First one, the polymer may be a matrix that stabilizes the nanoparticles growth and prevents nanoparticles agglomeration. Second one, the nanoparticles can be deposited in polymer matrices to improve some properties of the polymer as Raman activity, electrical conductivity, etc. or to modify the polymer structure, as its electronic structure, mechanical properties and electrical properties. Conductive polymers such as polypyrrole, can lose their conductivity over time, but with loads of nano-metals this property can be permanently. [Abdullah Alqudami, S. Annapoorni, P. Sen, R.S. Rawat., Synthetic Metals 157 (2001) 53-59]. In this paper we study the physicochemical properties of the composite nanoparticles of TeCd embedded in a polymeric matrix of PPy. The composite material is characterized by FTIR-ATR, SEM, and X-ray fluorescence.

# Experimental

## Synthesis of TeCd nanoparticles

Initially, is prepared a solution of  $CdCl_2$  and thioglycolic acid, TGA, at room temperature with constant molar ratio Cd/TGA of 1:6 and pH value was adjusted to 5 using a 3M NaOH solution. The Cd/Te molar ratio was varied from 1:3 to 4:1. At room temperature, under N<sub>2</sub> flow, NaHTe solution was transferred and the reagents were mixed until telluride precursor dissolved completely. The mixture was heated at 92°C under open-air conditions and during the first 20 minutes of initiate the reaction, the luminescence began to appear, due to confinement effects, and slightly green luminescence can be observed under illumination with a wavelength of 366 nm. With greater growth time, the luminescence of solution becomes more intense, and shifted to red due to the growth of nanocrystals.



Fig.1 Experimental setup.

# Preparation of the composite PPy-I film/nTeCd nanoparticles

The plasma reactor used to deposit a thin film of polypyrrole-iodine, PPy-I, is shown in Figure 1. The reactor consists of a glass tube of 90mm outside diameter with two stainless steel lids. The electrodes of the reactor are connected to a radio frequency of source, CESAR-1500, at 13.56

MHz and a power of 30W. The time of synthesis of each thin film layers of PPy-I was 30 minutes, every 10 min of reaction iodine valve was opened 4 min. Once the first layer deposited on a glass substrate, 2.5x2.5cm on deposit it a few drops of nanoparticle TeCd solution, after dried in a vacuum oven for 30 min. To deposit the second layer of PPy-I, the process was repeated until we have 2,3,4,5, and 6 layers of PPy-I with nanoparticles TeCd between each layer of PPy-I.

# Characterization and Discussion Analysis FTIR-ATR

The Fig. 2(a) show the infrared spectrum in ATR mode of PPy-I and in Fig. 2(b) is show the FTIR-ATR spectrum of the composite PPy-I/nTeCd with 6 layers of PPy-I. Both spectra show broad bands and complex characteristics of the materials synthesized by plasma. In 2(a) can see the PPy classic peaks. At 3327cm<sup>-1</sup> shows the vibration of the primary and secondary amine groups. The peak centred in 2976cm<sup>-1</sup> represents the vibration of the aliphatic carbons, CH2. The peak of 2181cm<sup>-1</sup> is an indication of the breakdown of the aromatic ring and is a signal of crosslinking of the polymer material. 1677cm<sup>-1</sup> corresponds to the amine groups of the structure of pirrrol while 1574cm<sup>-1</sup> is due to vibration in the plane of the C=C and C=N of the pirrrol structure. Two peaks observed at around 1374cm<sup>-1</sup> and 1036 cm<sup>-1</sup> can are attributed to vibration and breathing in plans of pyrrole rings, respectively. In Figure 2 (b) shows the FTIR-ATR spectrum of the composite with 6 layers of PPy-I. The band centered at 2164cm-1 is the most intense and possibly due to the interaction of TeCd nanoparticles with the polymeric material.



Fig 2 (a) FTIR-ATR spectrum of PPy/I. 2(b) composite of PPy-I/nTeCd with 6 layers.

# **Fluorescence Analysis**

The absorption spectra were measured on a Perkin-Elmer spectrometer WMS Lambda-5 model. This model is equipped with two lamps, a tungsten-halogen and other of deuterium, both allow to obtain an absorption spectrum in a range from 190 nm to 900 nm, in crystalline and amorphous solids.

For the emission spectra of each sample, is used a Perkin-Elmer fluorometer U-5, equipped with a pulsed xenon lamp and 10 ps pulse width and 10W. The light from this lamp is collimated by a mirror and reflects it towards the entrance of a monochromator, which is used to select the wavelength of the light incident on the sample. The Fig 3(a) show the emission spectra, the main peak is centered in 450 nm that corresponds to blue emission. The second peak is in 511nm and corresponds to green emission. In the spectrum of 3(b) the main peak is in the UV region.



Fig. 3 (a) Emision spectra of PPy-I/nTeCd, and (b) Exctation spectra of PPy-I/TeCd.

### **SEM Analysis**

Fig. 4 shows two micrographs of the composite at different magnifications, 4(a) with three layers of PPy and 4(b) with four layers of PPy. In both images large globular formations including a large number of small spherical formations are seen. It is possible that these spheres are formed by agglomerates of TeCd nanoparticles. Figures 4 (d and e) show the elemental analysis by EDS of the film three and four layers, show that it has Cd and iodine in varying amounts.



Fig. 4 SEM and Elemental analysis of composites

### Conclusions

Multilayer composites of CdTe nanoparticles and plasma PPy were made, they keep the photoluminicent properties of the components and aloud to form films with the properties of the

nanoparticles, they are dispersed in small domains as the SEM images show and this generates a composite material with potential applications to active elements in semiconductors and luminisent divises.

### Acknowledgement

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# **OBTAINING IRON-GOLD MAGNETIC NANOPARTICLES**

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### Abstract

In this work, iron-gold nanoparticles were obtained in two steps by employing ferrocene and tetrachloroauric acid at three different temperatures and relations (25-75, 50-50, 75-25%). The obtained samples were characterized by both UV-vis and Scanning Electronic Microscopy (SEM). On the UV-vis is observed the characteristic band of the gold (Au) whereas the micrographs shows particle diameter sizes of approximately 47 nm.

## Introduction

Magnetic nanoparticles (MNp's) are a major class of nanoscale materials that could be used as clinical diagnostic and therapeutic techniques [1]. Their applications are widely studied including magnetically assisted gene therapy, magnetically induced hyperthermia and magnetic-force-based tissue [2]. Due to their unique physical properties and ability to function at the cellular and molecular level of biological interactions, MNPs have been actively investigated in targeted drug delivery [3, 4]. Great efforts have been made in the fabrication of metallic nanoparticles that contain transition metals, alloys and metallic oxides which have been obtained from chemical synthesis such as reduction, oxidation or decomposition in aqueous or organic media. In the field of biology is desired the biocompatibility and interfacial reactivity of particles. One of the most attractive systems is iron-gold core-shell metallic particles. Gold and Ferric oxides are highly compatible with the human body, they are easy to detect and are functional for organic and bioorganic molecules such as proteins, enzymes and bacteria [5].

# Experimental

### **Obtention of iron nanoparticles**

For further combustion, ferrocene was diluted in ethanol in a metallic recipient under constant refrigeration. In order to avoid losses, magnetic additives are employed to maintain the particles adhered to the metal surface. The production time of these nanoparticles was evaluated between 3 to 5 hours depending on the employed alcohol quantity. Once the reaction was finished, the nanoparticles were removed from the surface avoiding air flows. At the end of the removal, nanoparticles were stored in a container in order to prevent any humidity that could affect their performance for future uses.

# **Obtention of iron-gold nanoparticles**

Experimental conditions such as temperature and relations of ferrocene/tetrachloroauric acid for obtaining Fe core/ Au shell nanoparticles are shown in Table 1.

	T1/°C	T2/°C	T3/°C
25/75	T1-25	T2-25	T3-25
50/50	T1-50	T2-50	T3-50
72/25	T1-75	T2-75	T3-75

Table 1 Experimental conditions

A general method of synthesis [6] was made in an extraction cabinet using a glass reactor with four entries under constant agitation. The container involved a gas valve to keep an inert atmosphere. The cap was firmly adjusted by a seal whose diameter is the same than the reactor. Toluene was added at 110°C. Ammonium tetrapropyl bromide was added to the solution, then it was mixed and sealed immediately once the temperature was reached. A HAuCl<sub>4</sub> solution was added for 15 minutes until the acid was transferred to the organic layer. Decanothiol was also added as stabilizer with NaBH<sub>4</sub> by employing a funnel in order to facilitate its remotion from the reactor wall.

Such addition produced a color change in the reactions and an overproduction of gases. Agitation was carried out for 3 hours maintaining a constant nitrogen flow since the beginning.  $Fe_2O_3$  nanoparticles were incorporated to avoid the losses to the atmosphere. The solution was agitated two more hours. Finally, reaction was cooled for pouring and stored.

UV-vis Spectroscopy was employed for characterization of Fe/Au nanoparticles. In the case of the sample T3-50, it was found a characteristic band related to gold in the wavelenght of 550 - 600 nm. Nanoparticles have a tendency to form agglomerates as shown by SEM micrographs (Figure 1). This fact suggests that the nanometric size difficults the analysis of the particle shape.



Figure 1. SEM image of Fe/Au with a resolution of 20000X

A particle of 30 nm was isolated with an approach of 300000X. A more defined particle in a hexagonal crystalline array was observed (Figure 2). In addition, vertical channels were formed in the cross section. A well-defined structure in the particle is assumed as a successful choice in synthesis. However, in this study the same particle shape is not uniformly obtained for all the analysis. On the other hand, an average particle size of 47 nm was found.



Figure 2. SEM image of Fe/Au with a resolution of 300000X

In Figure 3 each present element in the particle was denoted by remarking with red the iron presence and with blue the gold presence. Images were overlapped in order to observe the properties that are present in the experiment with more detail and analyze them, this is shown in Figure 4.



Figure 3.Presence of Iron (red) and Gold (blue) in the nanoparticle at 10000X



Figure 4. Overlapped images to observe the Fe/Au presence

In Figure 4, the recovering of Fe/Au was observed. Results are satisfactory according to the employed experimental method.

### Conclusions

Experimental studies revealed the obtention of Fe/Au nanoparticles with stable structures with an average size of 47 nm. The best sample was obtained with the highest proposed temperature and an intermediate relation.

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# EFFECT OF NA-MONTMORILLONITE SLURRY ON THE MECHANICAL, THERMAL AND RHEOLOGICAL PROPERTIES OF AN UNSATURATED POLYESTER RESIN

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It is well-known that nano-layered silicates and nano-clays possessing high surface to volume ratio, improve the mechanical properties of the polymer-nanoclay system, if they achieve a degree of intercalation or exfoliation.

Although the nanoclay is usually chemically-modified to make it organophilic and compatible with the polymer matrix, untreated montmorillonite was also used, taking advantage of its high swelling capacity in polar liquids like water or alcohol, allowing the expansion of the interlaminar spacing and the subsequent intercalation or exfoliation of the clay after polymerization. Exfoliation of montmorillonite in the polymer matrix has been shown to occur through a process called "slurry compounding", in which the montmorillonite swells in water, and then is mixed with polymers [1]. Other techniques include the addition of montmorillonite to water and subsequently the replacement of water by an alcohol or acetone with further addition of a silane agent to modify the clay and make it compatible with the polymer matrix [2,3].

In this work, preparation of nanocomposites using the the slurry system (MMT dispersed in water) is implemented to obtain polyester resin-clay nanocomposites. The paper includes the analysis of the influence of montmorillonite slurry on the cross-linking reaction with the unsaturated polyester resin, and the effect of the clay on the mechanical, thermal and rheological properties of the resulting nanocomposites. In addition, changes with respect to the pristine polyester resin in the gelation temperature and morphology of the nanocomposites prepared with this novel method are analyzed in detail.

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# **GRAPHENE OXIDE MODIFICATION WITH GRAFT POLYMERS**

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### Abstract

The chemical modification of graphene oxides is a rapidly growing area of graphene research since the approach provides an effective methodology for the design of new graphene materials, their possible exfoliation to soluble or dispersible fragments or sheets of graphene as well as of the oxide and the control of their properties. Moreover, chemically modified graphene and graphene oxides are expected to find a variety of possible applications in high-performance hybrid polymer nanocomposites and nanocomposite-polymer materials. The reaction of two graft polymerizations onto graphene oxide involving polystyrene (PS) and polyisoprene (PIP) will be discussed along with the characterization of the resulting materials. Graphene oxide was functionalized using 1-oxo-2,2,6,6-tetramethylpiperidinium (TEMPO) bromide (ammoniumsalt) in dimethylformamide (DMF) in the presence of triethylamine and characterized accordingly. The graft polymerization of styrene was performed via nitroxide mediated radical polymerization (NMRP) by a unimolecular initiation system in which the functionalized graphene oxide acts at the same time as a macroinitiator and potential controller. The reaction was performed by dispersion of the GO-TEMPO in DMF at 130°C in the presence of monomer to form graphene oxide-g-polystyrene-TEMPO (GO-g-PS-T). Reactions and characterizations were followed by FT-IR, TGA, XRD, EDAX and AA/ICP.

### Introduction

Graphene Oxide (GO) is a material consisting of carbon, oxygen, and hydrogen in variable ratios that may be obtained by treating graphite with strong oxidizers. When completely exfoliated, GO is a two-dimensional sheet of  $sp^2$  and  $sp^3$  hybridized carbon atoms, basically one atom thick. Upon chemical reduction, for example, GO may be reduced to graphene (G), which, in its purest form, is defect free and consists only of  $sp^2$  hybridized carbon with no bonded oxygen or hydrogen atoms. The remarkable physical properties of graphene, such as its unprecedented carrier mobility, have stimulated interest not only in new fundamental science, but also in applications such as electronics, optoelectronics, and biological sensors [1-2]. The understanding of the chemistry of graphene and its oxides lags far behind that of its physics and offers vast exploratory potential for the development of new materials and their applications. For example, GO has been subject to covalent modification with polymers resulting in new hybrid graphene/polymer nanocomposites [2-3]. When polymer chains are incorporated by bonding to modified or precursor GO, a material can result consisting of a polymeric matrix with GO embedded in it. Such incorporations can significantly alter and improve the physical properties of host polymers at extremely small loadings [2]. In the present study, we embedded GO in a styrene polymer matrix using a nitroxide mediated radical polymerization (NMRP) of styrene monomer and a modified graphene oxide previously functionalized with 1-oxo-2,2,6,6-tetramethylpiperidine (TEMPO) groups. The functionalization of GO with TEMPO was carried out in a DMF dispersion in the presence of triethylamine and the bromine oxoammonium TEMPO salt, previously synthesized according to Bonilla-Cruz et. al. [4-5].

# Experimental

### **Graphite oxidation**

Graphite powder from National (2 g) was put into cold (0°C) concentrated H<sub>2</sub>SO<sub>4</sub> (46 mL).

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KMnO<sub>4</sub> (6 g) was added gradually with stirring and cooling to keep the reaction mixture form reaching 20°C. The mixture was then stirred at 35°C for 2 h, after which distilled water (92 mL) was added. In 15 min, the reaction was terminated by the addition of a large amount of distilled water (280 mL) and 30%  $H_2O_2$  solution (5 mL), after which the color of the mixture changed to bright yellow. The mixture was filtered and washed with a 1:10 HCl/water solution (200 mL) in order to remove metal ions, then washed with water until neutral pH. The resulting GO dispersion was suspended in a mixture of ethanol and water to further exfoliate the GO through ultrasonication for 1 h and dried at 80°C [7].

# Synthesis of Br-TEMPO salt

The synthesis of the Br-TEMPO salt (Figure 1) was reported previously by Bonilla-Cruz et. al. [5]. In a typical experiment, bromine (0.032 mol) was added slowly to a solution of TEMPO in CCl<sub>4</sub> (0.032 mol in 100 mL of CCl<sub>4</sub>). A brown solid formed almost instantaneously and was separated from the solution by filtration. A small amount of additional bromine was added to obtain a yield of 90%. The filtrate was thoroughly washed with CCl4 until the filtered solution showed no color. The Br-TEMPO salt was dried under vacuum at 40 °C for 24 h [4-5].

# Graphene oxide functionalization reaction

The previously prepared GO (0.4 gr) was dispersed in 400 mL of DMF. A solution of Br-TEMPO salt (0.0156 mol in 40 mL of DMF) was added dropwise to the dispersion in the presence of triethylamine (0.0234 mol) utilized to trap the HBr formed during the reaction. The reaction system was then saturated with argon and stirred for 48 h at room temperature. The functionalized GO, GO-T, was purified by centrifugation and washed with DMF several times in order to remove the residual Br-TEMPO. The GO-T was then lyophilized for 24 h. The GO and GO-T were analyzed by XRD, Raman spectroscopy, and TGA.



Figure 1. Schematic illustration of the functionalization reaction and graft styrene polymerization.

# Graft styrene polymerization

The polymerization of styrene was conducted in a 25 mL glass reactor; GO-T (0.024 gr) dispersed in 24 mL of DMF and then styrene (1 mL, 0.9 g, 0.0086 mol) were added to the reactor with stirring. The reactor temperature was then raised to 130°C. After five hours of reaction, the polymerizations were stopped. The dispersion was then centrifuged and washed with DMF. To separate styrene and the free polystyrene from the graphene oxide-g-polystyrene-TEMPO (GO-gPS-T), the suspension was centrifuged, washed with DMF, and precipitated with methanol. The GO-g-PS-T was dried for FT-IR and TGA analyses.

### **Results and Discussion**

The Br-TEMPO salt is stable. A proposed functionalization reaction mechanism is discussed by Bonilla-Cruz et. al., although the nature of the bond linking the oxygen from the TEMPO moiety to a substrate containing OH groups is still a subject of debate [4-5]. Comparing the elemental analysis data of the as-prepared GO (C: 40.08%, H: 2.71%, O: 46.71%) with GO-T (C 52.6%, H 3.88%, O 35.21%, N 3.36%), the latter showed an increase in N of 3.36% due to the incorporation of the TEMPO groups.

# **X-Ray diffraction**

XRD patterns of GO (black line) and GO-T (red line) are shown in Fig.2. The shift in the main peak to low angles in the GO-T indicates a larger layer-to-layer separation in the GO-T material consistent with the larger TEMPO group.



Figure 2.XRD analysis of GO (black line) and GO-T (red line).

# Raman spectroscopy

The Raman data (Fig. 3) for GO (black) and GO-T (red)show a D band to G band intensity ratio of 0.688 for GO and 0.793 for GO-T consistent with more disorder in the GO-T layers and probably due to a decrease in the number of in-plane  $sp^2$  domains [3].



Figure 3.Raman spectral analysis of the GO (black line) and GO-T (red line) materials; G band is on the left.

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### **FT-IR** Analysis

The GO, GO-T, and GO-g-PS-T were analyzed by ATR FT-IR. Figure 4A shows the characteristic vibrations for GO with strong bands in the 3000–3700 cm<sup>-1</sup> and 1000-1100 cm<sup>-1</sup> regions, which correspond to the stretching vibrations of intermolecular hydrogen bonded –OH and C–O groups, respectively, as well as stretching vibrations at 1650 and 1726 cm<sup>-1</sup> due to the carbonyl groups. The small new peaks at 2966 ( $\nu$ , CH<sub>2</sub>) and 2900 cm<sup>-1</sup> ( $\nu$ , CH<sub>2</sub>) regions for GO-T (Fig 4B) are attributed to asymmetrical and symmetrical stretching of the aliphatic carbons from TEMPO. Additionally, a new peak near 1421 cm<sup>-1</sup> is attributed to the asymmetrical bending vibration of the methyl groups ( $\nu$ , CH<sub>3</sub>) of TEMPO. GO-g-PS-T (Fig 4C) shows characteristic GO peaks in addition to new absorption bands in the 3000–3100 cm<sup>-1</sup> and 2980–2850 cm<sup>-1</sup> regions, which correspond to aromatic stretching vibrations (ns, C–H) and the methylene stretching vibrations (n, CH<sub>2</sub>) from styrene [4].



Figure 4.ATR FT-IR spectra of a) GO (black), b) GO-T (red), and c) GO-g-PS-T (blue) materials.

### Thermogravimetric analysis

TGA data for GO, GO-T, and GO-g-PS-T are shown in Fig 5. Figure 5a revels a loss of 12.9 wt.-% which is attributed mainly to the loss of physisorbed water. The second loss (28.39 wt.-%) and a change in slope of the derivative (max 216°C) is attributed to the decomposition of functional groups like C=O or OH. GO-T (Fig 5b) also shows a change in slope of the derivative (170°C) which is attributed mainly to the decomposition of TEMPO. Figure 5c shows a loss attributed to the degradation of the organic material grafted to the GO [4-5].



Figure 5.TGA data for a) GO, b) GO-T, and c) GO-g-PS-T

### Conclusions

The graft polymerization of styrene on modified graphene oxide was carried out by a nitroxide mediated radical polymerization to form a new nanocomposite material consisting of a styrene polymer matrix with embedded graphene oxide. The synthesis is carried out via a unimolecular initiation system using the 'grafting-from' technique, starting from a graphene oxidepre-functionalized with TEMPO groups. The GO-T material acts as a macroinitiator and potential controller. The success of the reactions demonstrated herein between GO-T and monomers like styrene and isoprene suggest a general preparative route for the preparation of graphene oxide embedded polymer nanocomposite materials. Moreover, the GO-g-PS-T and GO -g-PIP-T may be considered as possible precursors to the preparation of the potentially important graphene analogs, G-g-PS and G-g-PIP, by reduction.

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# GRAFTING OF ITACONIC ACID INTO POLYETHYLENE AND NANOPARTICLES DISPERSION AND EXFOLIATION APPLYING ULTRASOUND DURING REACTIVE EXTRUSION

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### Abstract

The funcionalization of Polyethene (PE) by grafting itaconic acid (IA) using reactive extrusion, was studied. This was done in a twin screw extruder applying ultrasound that would act as the reaction initiator and would enhance the nanoparticle dispersion in the PE/Clay composites, as well. Three ultrasound intensities were used, and samples were directly fed into the extruder to be processed, functionalized and dispersed in one step along the extruder. The obtained nanocomposites were characterized by FTIR that confirmed the IA grafting into PE and by titration determinations the grafting efficiency was determined. All nanocomposites treated with ultrasound showed better intercalation and exfoliation compared with the nanocomposites without ultrasound treatment. The results of mechanical properties, X-Ray diffraction and transmission electronic microscopy showed that the grafting degree, exfoliation and mechanical performance depend on IA concentration, processing temperature and ultrasound intensity as compared with untreated composites.

### Introduction

It is well known that the incorporation of nanoclays in a polymer matrix improve or modify some specific properties of the polymer. Polymer nanocomposites have become in a new type of hybrid composites (1,2). In the last few years, polymeric composites with nano particles of silicate clay, such as montmorillonite, have been widely studied mainly because of their improvement in tensile modulus, tensile strength and heat distortion temperature compared with the original polymer [3]. Chemical modification of some polymers to include polar groups that could increase the interfacial interaction between polymer - nanoparticles and enhance the physical properties [4,5]. In polymers, ultrasound has been used in polymerization and depolimerization reactions, molecular weight control and synthesis of graft and block copolymers [6]. On the other hand, applying ultrasound in polymer melts is an effective method to improve dispersion, intercalation and exfoliation of nanoclays in polymer nanocomposites during reactive extrusión[7,8].

# Experimental

### Materials

The polymer matrix used was low-density polyethylene (LDPE 22004) from PEMEX, with an MFI of 0.4 g/10 min, which is a homopolymer recommended for the production of high-strength packaging, which offers a combination of good visual appearance with excellent mechanical resistance, maximum resistance to environmental fracture (ESCR). For Nanocomposites preparation Cloisite 20A nano clay was provided by Southern Clay Products Co. Ultrasound was used for enhance its dispersion and exfoliation and also as an initiator of the grafting reaction. A monomer of IA form Aldrich was used as compatibilizer, which is a carboxylic acid white Crystal obtained by the fermentation of carbohydrates. It contains two double bonds combined with the carbonyl group.

### **Preparation of compounds**

A co-rotating WERNER & PFLEIDERER ZSK-30 twin screw extruder was used for preparation

of composites, it was assisted with an ultrasound (US) device (Cole Palmer- 750) located in the die head, with a maximum power output of 750 watts at 20 kHz with a flat temperatures profile.



Figure 1. Chemical structure of Itaconic acid.

This provided the breakdown of the agglomerates and simultaneously promotes a grafting reaction between Itaconic acid and polyethylene since the ultrasonic energy is capable of generate free radical formation. Screw speed was 50 rpm. In this way, clay dispersion can be enhanced and polyethylene chemical modification promoted and thus obtaining polyethylene-clay nanocomposites. Clay concentration was constant at 5wt%. Type of clay, ultrasound energy, temperature of processing and clay content are described in the following table.

_	Conc. Itaconic Acid (%w)	Processing Temp.,(°C)	US Intensity, watts (%)
_	1.0, 3.0	185, 200, 210	231(60),346 (45), 462 (60)
_			

 Table 1. Components contens, US energy and processing temperature for preparation nanocomposites by extrusion.

### Specimens preparation and characterization

Plaque samples of 3 mm thickness were obtained by compression molding at 160°C for 5 min. Then samples for DRX characterization were prepared from these plaques. Mechanical properties were characterized using ASTM D790 standar. For the characterization by FTIR of the IA grafting degree, 1 g of material was dissolved in 250 ml of xylene at 120 ° C to remove the non reacting IA where a film is subsequently prepare for fusion. The determination of the content of graft of IA and then a melt film was prepared. In addition grafting degree was calculated using a titling method as reported in the literature [9]. Samples were characterized by differential scanning calorimetric (DSC) and thermo gravimetric analysis (TGA). Nanocomposites morphology was determined by transmission electron microscopy (STEM).

### **Results and Discussion**

X-ray diffraction technique is very useful to characterize Nanocomposites based on polyolefins using compatibilizer agents by determining the degree of exfoliation of the organo-clay [10]. Thus, if the signal of d001 clay diffraction in a nanocomposite disappears, a complete exfoliation is obtained. On the other hand, if diffraction d001 peak only decreases and moves towards lower  $2\theta$  angles, it is an indication of an intercalation and/or partial exfoliation in the nanocomposite [11]. This has been found for the majority of the polyolefins using a compatibilizing agent between the nanoclay and the polymer. Figure 1 shows the diffraction patterns of C20A clay and reference samples with 1 and 3 wt % of Itacónico acid (IA) at the three considered temperatures without applying Ultrasound (US). It can be seen that all samples where IA was used as compatibilizer show a shift towards smaller angles indicative of some degree of intercalation and clay dispersion. Even that all samples shifted to smaller angles the samples that presented lower peak intensity were those with lower IA content and prepared at 215 ° C. The shift of the peak towards smaller angles and the decrease in the intensity of the peak indicate that a more dispersed and intercalated structure was obtained. Thus a lower US intensity indicates lower arrangements of galleries indicative of a greater disorder in them. This shift, even small, to lower

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angles when no US was applied, could be attributed to a certain amount of IA can be grafted by the mechanical stress that is generated during the processing of the samples at high temperatures. These conditions can promote the breakdown of the polymer chains and generate free radical where the graft of IA in the polymer chain is feasible. Figure 2 shows the XRD patterns for the samples prepared at different temperatures and US intensities with 1 wt % of IA. All the samples presented a shift towards lower angles indicative of certain degree of clay dispersion and intercalation. Intermediate US intensities, 45 to 60%, and temperatures higher than 215°C showed, beside the shift of the peak towards lower angles, a notable decrease on this peak intensity. This can be attributed to the fact that higher temperatures reduces the viscosity of the polymer matrix which promote a wider diffusion of the US through the melt and allowing a higher US incidence in the breaking of chains and the grafting of the functional group, which is widely reported [12].



**Figure 1.** XRD patterns of nanocomposites with 1% and 3% of IA At differents temperatures without US.



Figure 3 shows the micrographs for Nanocomposites prepared with 3% of IA at 215 °C and with 462 watts (60%) of US intensity for samples with 5% of clay. Tactoides and clay aggregates can be observed which coincide well with XRD results in which at this IA content a good dispersion of the clay were not achieved. This behavior may be attributed to the excess of free IA which could interact with the surface of the clay and saturate the available free sites in which the polymer could penetrate and interact with the clay to promote its exfoliation. Figure 4 presents STEM images for nanocomposites now prepared with 1% of IA. A better degree of clay dispersion and intercalation was obtained when using this IA content compared with the image for the 3% of IA. A lower amount of tactoides can be seen in these samples, appreciating only few clay agglomerates. These results coincide well with those obtained for XRD results where a greater displacement of the diffraction peak was obtained for this IA content.



**Figure 3.** STEM Micrograph of nanocomposite with 3 % of AI and 462 watts (60%) US at 215°C.

**Figure 4.** STEM Micrograph of nanocomposite with 1 % of AI and 462 watts (60%) US at 215°C.

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Figure 5 shows the weight loss for the material depending on the applied temperature, as well as the effect on the thermal stability of the Nanocomposites at different US intensities. Pure PE shows a less thermal stability compared with compounds with 5% of clay at different US intensities. Samples prepared at 462 watts (60%) of US have a slight greater thermal stability in comparison with those prepared at 231 Watts (30%) and 346 watts (45%) of US. This could be attributed, as was already mentioned, to the higher effect of US intensity in grafting IA in to the polymer chain. Because is reported that a better degree of intercalation or exfoliation can promote a higher thermal stability. This is attributed to the better barrier that present the exfoliated and dispersed clays towards the diffusion of gases such as oxygen for combustion as well as the gases produced during combustion [13]. The FTIR spectrum obtained from the compound with 1% of AI, processed 185 ° C without ultrasound and with an US intensity of 462 watts (60%), can be seen in Figure 6. FTIR spectra for sample without US (20A, 1% of AI, 185 ° C without US) does not show any band at 1715 cm - 1 indicating that no grafting of AI in LDPE was achieved. On the other hand, compounds with ultrasound (3% of AI, 185 ° C, 462 watts (60%) of US) show notorious carboxylic bands of the of IA at 1715cm-1 indicating that the grafting of IA in LDPE was achieved. Table 2 shows the IA content grafted into LDPE determined by titration in which a higher content can be observed for the 3wt% sample.

Sample	IA Grafting (%)
3%AI - 185°C - 60%US	0.9048
1%AI - 215°C - 30%US	0.4549
	$\mathbf{D}\mathbf{\Gamma} = 1 \cdot 1 = 1 1 \cdot 1 \cdot 1$

**Table 2.** IA grafting in LDPE obtained by titration.

Behavior of the flexural modulus for the nanocomposites with C20A and I28E clay depending on the US intensity at different temperatures can be seen in Figure 7. A trend towards the increase of modulus with the US intensity for all compounds can be observed. Also can be seen a slight increase in modulus depending on the processing temperature for samples with and without ultrasonic treatment. This can be due to the reduction on melt viscosity, promoting a higher clay dispersion in the polymer. It is also noteworthy that compounds with 1% of IA presented modulus values greater than those containing 3% of IA. Even though the extent of graft is greater in the case of the compounds with 3% of AI, this behavior is due to the increased amount of free IA without reacting that exists in these compounds that can act as a lubricant or plasticizer that decrease properties.



Figure 5. TGA curves of nanocomposites (a) LDPE; (b) 1 % IA 215°C 40% US; (c) 1% IA 215°C 60% US.

**Figure 6.** FTIR Spectra of nanocomposites with different IA content and the same processing temperature and US..

These results corroborate what was observed in DRX and STEM, where the greatest increase in the intergallery spacing was observed and from STEM images a better intercalation - exfoliation structure was observed.



**Figure 5.** Modulus of nanocomposites with 1% IA and 3% IA at 185°C of processing temperature with Different Intensities of US.

**Figure 5.** . Modulus of nanocomposites with 1% IA and 3% IA at 215°C of processing temperature with Different Intensities of US.

# Conclusions

In this work PE/clay nanocomposite materials were obtained by in situ functionalization of PE with IA and at the same time dispersing the nanoclay by using ultrasound vibrations with an acceptable grafting degree and good clay dispersion and intercalation as well as an acceptable physical-mechanic performance.

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# LAYER BY LAYER HYBRID GRAPHENE OXIDE POLYELECTROLYTE MULTILAYERS - SELF ASSEMBLY AND TRANSPORT

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### Abstract

Exfoliated graphene oxide (GO) sheets were functionalized with quaternary ammonium groups by nucleophilic substitution of amines on the GO epoxy and hydroxyl groups to form the cation functionalized graphene oxide,  $GO^+$ , with iodide as the counter ion. Confocal Raman Microscopy (CRM) and XPS were used to characterize the graphene oxide functionalization.  $GO^+$  sheets were assembled as cationic components in polyelectrolyte multilayers by means of the Layer by Layer (LBL) technique, intercalating layers of poly allyl amine hydrochloride (PAH) and poly sodium styrene sulfonate (PSS) to form a thin hybrid multilayered film [1]. The quartz crystal microbalance with dissipation (QCM-D) and CRM were used to follow the stepwise assembly of the  $GO^+/PSS/PAH$  multilayers. By means of QCM-D the amount of  $GO^+$  assembled per layer was quantified [2]. Also, the influence of the number of layers of PSS/PAH between two layers of  $GO^+$  on the amount of  $GO^+$  assembled was studied by QCM-D. Surface topology of the hybrid  $GO^+/polyelectrolyte$  multilayer was characterized by AFM. Finally, the influence of the  $GO^+$  on the transport properties of the layers was investigated by fluorescence techniques.

### Introduction

Controlling the composition and properties of materials at the nanoscale is a key scientific and technological issue. Many of the applications of nanotechnology are associated with the development of complex materials in which nanoparticles or nanomaterials are integrated, and whose functionalities and properties are enhanced or tuned by the nanocomponents.

The layer-by-layer (LBL) technology is based on the sequential adsorption of polyelectrolytes on a charged surface to form thin polymer films with controlled properties at the nanoscale. LBL can be applied for the fabrication of hybrid materials, including nanoparticles, viruses, lipids layers, and carbon nanotubes, which are assembled at the place of selective layers, provided that these are electrically charged. In general the LBL technique provides the means for the fabrication of films and devices with a controlled composition at the nanoscale whose complexity can be increased by the sequential deposition of new components [1].

There is, on the other hand, much interest in obtaining homogeneous coatings based on graphene (G) or graphene-like materials, such as the more chemically addressable graphene oxides (GO), which can be subsequently reduced to form a more defect free graphene. Such materials could be used for surface functionalization or, more importantly, to integrate graphene or graphene-like layers into chemically, electronically, biologically or optically active devices for a host of applications. The LBL technique, in combination with graphene or graphene oxide, for example, can provide active multilayer structures that can be used in electronics as transparent electrodes, capacitors and protective applications. The sequential character of the LBL assembly makes it possible to incorporate other materials into or proximal to the G and GO layers, such as quantum dots or metal nanowires, at defined distances from the active monolayers to further tune the properties of the active layers.

The scope of this work is to show the integration of ionically charged graphene oxides into LBL

films and to study the mechanism of assembly of the GO and polyelectrolytes. The quartz crystal microbalance technique was used to follow the assembly of single sheet ionically substituted GO layers. The GO layers were alternated with a variable number of layers of polyelectrolytes in between.

# Experimental

# Preparation of graphene oxide

Graphite powder from Aldrich (2 g) was put into cold (0°C) concentrated  $H_2SO_4$  (46 mL). KMnO<sub>4</sub> (6 g) was added gradually with stirring and cooling to keep the reaction mixture form reaching 20°C. The mixture was then stirred at 35°C for 2 h, after which distilled water (92 mL) was added. In 15 min, the reaction was terminated by the addition of a large amount of distilled water (280 mL) and 30%  $H_2O_2$  solution (5 mL), after which the color of the mixture changed to bright yellow. The mixture was filtered and washed with a 1:10 HCl/water solution (200 mL) in order to remove metal ions, then washed with water until neutral pH. The resulting GO dispersion was suspended in a mixture of ethanol and water to further exfoliate the GO through ultrasonication for 1 h and then dried at 80°C [3].

### Preparation of quarternary ammonim ion functionalized graphene oxide

100 mg of GO was dispersed in 10 mL of water, followed by the addition of 300 mg of methylamine in 10 mL of ethanol (Eq. 1). The GO solid swelled instantly upon addition of the amine solution. Mixtures were allowed to stir for 20 h at room temperature before isolation of the resulting derivative. This procedure was repeated several times to prepare one gram of sample. 500 mg of GO amine were then dispersed in 25 mL of N-methyl-2-pyrrolidone during 12h at room temperature. 65 mg of NaOH and 23 mmol of  $CH_3I$  were added to the dispersion. The reaction was carried out with stirring for 12 h at 50°C after which acetone was added to precipitate the desired product shown schematically in Figure 1. The methyl iodide used in the reaction provided iodide as the counter ion.

$$GO/H_2O + MeNH_2/EtOH$$
 (stirring, RT, 20 h)  $\longrightarrow$  GO-NH-CH<sub>3</sub> (GO-Alkyl amine) Eq. 1.



**Figure 1.** Amine (left) and quarternary ammonim ion functionalized graphene oxide (right). Counter iodide ions and unreacted OH, O and COOH groups for the latter were omitted for clarity. One CH<sub>3</sub> group and two H atoms constitute each R<sub>3</sub> in the cationic structure (right).

# LBL Assembly

LBL assembly of GO and polyelectrolytes was followed by the Quartz Crystal Microbalance (QCM-D) technique. While polyelectrolytes, poly (styrene sulfonate) (PSS) and poly(allyl amine) hydrochloride (PAH) were assembled in 0.5 M NaCl, the GO layers were assembled in millipore purified water to avoid screening of the GO charges. GO/polyelectrolyte films were assembled on top of a silica coated quartz crystal. Between the assembly of polyelectrolyte layers and the GO, the quartz crystal was rinsed with water several minutes. All the assembly and washings were done inside the QCM-D [2].

# Confocal Raman Microscopy (CRM)

CRM was used to follow the growth of the GO/polyelectrolyte film by recording the intensity of the G and D bands from the GO as a function of layer number. For these experiments up to three layers of GO were assembled with polyelectrolytes in between. Measurements were done with the 532nm laser and 50-X objective. GO shows typical D and G bands located at 1333 cm<sup>-1</sup> and 1582 cm<sup>-1</sup>.

# **Results and Discussions**

Graphene oxide was prepared by a modified Hummer's method, and subsequent amine insertion at the GO epoxy groups. The resulting N-alkyl graphene oxide was quaternized using methyl iodide. The degree of substitution of the N-methyl amine and the quaternized N-methyl ammonium graphene oxide was 2 mmol and 3.2 mmol, respectively.

In the FT-IR ATR spectra of graphene oxide and its derivatives there exist three characteristic peaks of graphene oxide: a strong and broad absorption at 3400 cm-1 due to O-H stretching vibrations and the peaks at1706 and1210 cm-1 ascribed to the C=O stretching vibrations. As the modification of graphene oxide proceeded, the intensities of amine and methyl peaks increased. Although marked differences were not observed from FT-IR spectra for the quaternized graphene oxide, the intensities of the peaks around 1460 and 705 cm-1, due to the presence of methyl groups, were increased with addition of  $CH_3I$ .

The XRD pattern of dried GO prepared here reveals a sharp peak corresponding to the c-axis spacing of 7.44 Å; this suggests intercalated water in the lamella of GO; the interlayer GO distance depends strongly on the GO:H<sub>2</sub>O ratio. When amine was inserted in the GO sheets, the layer-to-layer distance increased to 8.05 Å. When the cation was formed using methyl iodide, the layer-to-layer distance increased to 8.54 Å. All samples were dried before XRD runs.

The quartz crystal microbalance with dissipation (QCM-D) and CRM were used to follow the stepwise assembly of the  $GO^+/PSS/PAH$  multilayers. By means of QCM-D the amount of  $GO^+$  assembled per layer was quantified. QCM-D was also used to study the influence of the number of layers of PSS/PAH between two layers of  $GO^+$  on the amount of  $GO^+$  assembled.

CRM allows one to visualize the signal from the GO as the GO/polyelectrolyte system grows. As shown in Figure 2, films with a layer of GO deposited on top of three layers of polyelectrolyte, show the characteristic Raman G and D bands. Addition of a second layer of GO with three polyelectrolyte layers in between, increases the intensity of the G and D bands notably from around 1000 A.U to 3000 A.U. The addition of a third series of layers increases the total intensity to higher values, but not proportionally to the increase due to the second assembled layer. Interestingly, the G and D bands of the first and second layer of GO with polyelectrolyte on top show similar values. This may be related to either removal of GO through the polyelectrolyte or a change in the packing of the GO layers and deserves further studies. Since CRM is based on the intrinsic signal of the GO, the presence of the spectra and the changes observed along the

assembly proves that polyelectrolyte and GO can alternatively assemble [3]. Surface topology of the hybrid GO<sup>+</sup>/polyelectrolyte multilayer showed a homogeneous surface by AFM.



Figure 2. Intensity of GO G (left) and D (right) Raman bands as a function of the number of assembled layers.

# Conclusions

Exfoliated graphene oxide (GO) sheets were functionalized with quaternary ammonium groups by nucleophilic substitution of amines on the GO epoxy and hydroxyl groups to form the cation functionalized graphene oxide,  $GO^+$ , with iodide counter ion.  $GO^+$  sheets were assembled as cationic components in polyelectrolyte multilayers by means of the Layer by Layer (LBL) technique, intercalating layers of poly allyl amine hydrochloride (PAH) and poly sodium styrene sulfonate (PSS) to form thin, hybrid multilayered films. QCM-D, CRM and AFM data show the formation of hybrid multilayers with a continuous growth.

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# PREPARATION AND CHARACTERIZATION OF LOW DENSITY POLYETHYLENE BLENDS WITH MODIFIED CHITOSAN USING POLYLACTIC- ACID

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### Abstract

A series of polyethylene/chitosan composite films were prepared by extrusion using glycerol as a plasticizer and polyethylene-grafted-maleic anhydride as a compatibilizer. It was possible to obtain films with a maximum content of 20% chitosan. Polymers were characterized by FTIR, thermal analysis, SEM and tensile loading. The use of an anhydride-based coupling agent was effectively extended to improve the mechanical properties of chitosan composites.

## Introduction

Nowadays it is recognized that the use of synthetic polymers leads to environmental pollution, associated to the waste generated by plastic products. Currently these materials are widely used in containers or other types of disposable wraps for substances or articles, and these are discarded into the environment after use.

Waste biodegradable polymeric material products are capable of degradation when exposed to natural factors and water-soluble chemical reagents. A large group of these materials is based on biopolymers belonging to polysaccharides, as well as on their composites with synthetic thermoplastics. [1, 2]

This work aims to prepare mixtures including one of the most widely used synthetic polymers: polyethylene (PE), with biodegradable polymers such as chitosan [3] and polylactic acid (PLA), another component in these blends is modified chitosan using PLA.

Chitosan films have great potential to be used as packaging material due to their antimicrobial activity [4], nontoxicity and biodegradability [5, 6].

The major disadvantage of incorporating natural polymer into synthetic polymer is their compatibility. Natural polymers are hydrophilic while synthetic polymers are hydrophobic in nature. The resultant blend of these two types of polymers is almost immiscible [7].

The interfacial compatibility between chitosan and the thermoplastic matrix is a critical requirement for obtaining good mechanical properties in these composites. Several groups have proposed the use of compatibilizers as alternatives to strengthen the interface of immiscible blends [8].

# Experimental

During this first stage of the work several PE/chitosan mixtures were prepared; this included the use of glycerol as a plasticizer for the chitosan and Polyethylene-graft-maleic anhydride (PEgMA) as a compatibilizer for the blend.

## **Film preparation**

Chitosan was dried at 110°C for 24h before its use; the other components were used as received. Glycerol was selected as a plasticizer because of its plasticizing power, nontoxicity and thermal stability [1]. Table 1 indicates the concentration of each component on the prepared composite films. The glycerol/chitosan concentration ratio in the compositions was constant, 2g glycerol/g chitosan.

**Table 1.** Composites prepared by extrusion.

	Concentration in composites				
Code	Polyethylene (%)	Chitosan (%)	PEgMA (%)	<b>Glycerol</b> (g/g chitosan)	
PE	100	0	0	0	
PE5	95	5	0	0	
PEC5	90	5	5	0	
PECG5	90	5	5	2	
PECG10	85	10	5	2	
PECG15	80	15	5	2	
PECG20	75	20	5	2	
PECG30	65	30	5	2	

The polymeric blends were prepared in two stages: (1) mixing chitosan with the plasticizer to obtain a homogeneous mass and (2) mixing plasticized chitosan with LDPE and PEgMA.

The composites were prepared using an Atlas Laboratory mixer-extruder, the speed of rotation was 40 rpm, and the temperatures were controlled at 130 and 140°C for the rotor and the head respectively, except for the pure LDPE film, in this case, the temperatures were controlled at 115 and 125°C.

# Characterization

FTIR spectroscopy of the composite films was performed with a FTIR Perkin-Elmer 1600 spectrometer. The spectrum was scanned from 4000 cm<sup>-1</sup> to 370 cm<sup>-1</sup>. An average of 32 scans was recorded.

TGA and DSC were performed in a TGA-DSC unit from DTA; approximately 6 mg of sample was placed in the alumina pan at a heating rate of  $10^{\circ}$ C/min from room temperature to  $550^{\circ}$ C under air flow of 50 mL/min.

A typical specimen from each composition was selected, and the morphology of the surface was studied with a JEOL 5410LV scanning electron microscope. The samples were gold-sputtered before the scanning electron microscopy (SEM) examination.

The thickness of the film was measured with a Mitutoyo micrometer. The mechanical properties of the composite films were measured in a tensile loading mode with a United SSTM-5KN universal testing machine equipped with a load cell of 5 kN at a strain rate of 10 mm/min. At least eight specimens from each film were tested, and the average values are reported.

### **Results and Discussion**

### **Film preparation**

Using PEgMA as a compatibilizer and glycerol as a plasticizer it was possible to extrude composite films with chitosan in the range from 5 to 20% the films showed good processability and homogeneity; at 30% it was not possible to obtain the films.

### Thermal analysis

Fig. 1 shows weight loss and heat flow of the raw PE, chitosan and the prepared composites against temperature. The PE's melting point (Tm) can be observed at approximately 110°C. The PE's Tm is not affected by the presence of chitosan, glycerol or PEgMA. In Fig 1a thermal degradation starting at 250°C is detected; as for chitosan, a certain loss of water is observed (Approx. 4%), the thermal degradation of the material starts at 230°C.



Figure 1. TGA and DSC curves for PE (a), Chitosan (b), PE5 (c) and PECG5 (d).

### Morphology

Figure 2 shows the morphology of the surface of the extruded composite films. Qualitatively there are no differences in the surface of the composite films with chitosan ranging from 5 to 20%, chitosan particles coated by PE can be observed, and this indicates a good adhesion between PE matrix and chitosan. In Fig. 2e, the two phases are clearly observed. The results of the morphologic characterization corroborated the important role played by PEgMA in the compatibilization of the extruded composites of PE and chitosan.



Figure 2. SEM micrographs of the surface of (a) PECG5, (b) PECG10, (c) PECG15, (d) PECG20 and (e)PECG30.

### **Mechanical properties**

Figure 3 presents the Young's modulus, tensile strength, and the elongation at break of the films extruded from PE/5% PEgMA/chitosan polymeric blends vs. the chitosan concentration.

It can be observed that the Young's modulus increase with increasing chitosan concentration, this is a typical behavior for thermoplastic materials blended with brittle materials such as chitosan.

It is seen that the parameters tensile strength and elongation at break decrease with increasing chitosan concentration. This is due to an increase in their imperfection. Apparently, extension causes the composite samples to fail at the interface of PE and filler phases, and the surface area of the interfaces increases with increasing chitosan concentration.



Figure 3. Young's modulus (a), Tensile strength (b) and Elongation at break (c) of PE/5% PEgMA/chitosan film samples vs. chitosan concentration.
### Conclusions

Filling of polyethylene with chitosan, a biodegradable polysaccharide agent, sharply decreases the fluidity of the polymer. Introduction into this blend of a compatibilizer, polyethylene with grafted maleic anhydride allows easy processing of the polyethylene/polyethylene with grafted maleic anhydride/chitosan compositions into films on standard extrusion equipment.

The use of an anhydride-based coupling agent, extensively used to compatibilize polymer blends, for example, polymers that contain amide active groups, was effectively extended to improve the mechanical properties of chitosan composites.

The improvement in extrusion and the changes in the mechanical properties of the composites with PEgMA were interpreted as a consequence of the compatibilization effect of the coupling agent.

The improvement in the mechanical properties of the compatibilized films makes these compositions suitable for preparation of biodegradable polymeric materials intended for disposable applications.

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# MICROEMULSION POLYMERIZATION OF METHACRYLIC MONOMERS: EFFECT OF THE LENGTH OF THE ALKYL GROUP ON KINETICS AND COLLOIDAL PROPERTIES OF LATEXES

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#### Abstract

In this work, monomers of methyl- (MMA), ethyl- (EMA), n-butyl- (BMA), n-hexyl (HMA) and 2-ethyl hexyl (2-EHMA) methacrylates were homopolymerized in microemulsion at 60 °C using sodium dodecyl sulfate (SDS) as surfactant and potassium persulfate (KPS) as initiator. The effects of the monomer content in the reaction mixture (2.5 wt. % and 3.5 wt. %) and the length of the alkyl groups of the methacrylates on the kinetics and average particle diameter (Dp) were studied. For 3.5 wt. % of monomer concentration, at the beginning of reaction there is no significant difference in the polymerization rate, however, at high conversions, the order of polymerization rate were  $Rp_{EMA} > Rp_{BMA} > Rp_{2-EHMA} > Rp_{2-EHMA} > Rp_{MMA}$ , whereas for 2.5 wt. % of monomer concentration, the polymerization rate were  $Rp_{BMA} > Rp_{HMA} > Rp_{2-EHMA} > Rp_{EMA} > Rp_{MMA}$ . This behavior was ascribed to the differences in the water solubility and monomer partitioning between the different phases, as well as to monomers reactivities. Average particle size diameters, which were in all cases below 60 nm, increased with the hydrophobicity of each monomer.

#### Introduction

Polymer particles in the nanosize range appear to perform better than larger particles because their smaller size allow them to reach sites that cannot be reached otherwise, and because their greater surface/volume ratio gives them higher efficiency in those applications in which specific surface area is determining (Ledezma et al., 2007). Microemulsions are thermodynamically stable systems which are formed spontaneously by mixing an organic and an aqueous phase in the presence of a surfactant in the proper amounts (Shi et al., 2005). By microemulsion polymerization it is possible to obtain polymeric nanoparticles with diameters < 50 nm and polymers with high molar masses and a variety of microstructures, which influence polymer properties (Herrera et al., 2003).

Radical polymerization is one of the most widely employed methods for producing polymers because of its versatility and availability. However, the control of the stereochemistry is hard to attain because the growing radical species is a planar-like sp2-carbon, which induces a non-stereospecific propagation. It was reported that stereospecific addition could occur for monomers with bulky substituents, due to steric repulsion. With increasing bulky substituents in methacrylates and methacrylamides, rich-isotactic polymers were obtained by radical polymerizations.

Although the microemulsion polymerization of some alkyl methacrylates have been studied separately (Morgan et al., 1997; Tang et al., 2008), there are not reports addressed to find a correlation between the alkyl group length with the kinetics aspect and colloidal behavior. For example, Morgan (Morgan et al., 1997) reported a mathematical model developed to make a kinetics study about microemulsion polymerization of HMA. Their model predicts very well the conversion and polymerization rate through reaction but not the particle size and number. Besides, contrary to the experimentally observed, the model indicates that the maximum polymerization rate always occurs at conversions of 39%, independently of the monomer used. Tang (Tang et al., 2008) studied the effect of alkyl side group of some methacrylates as MMA, EMA, cyclohexyl

methacrylate, iso-butyl methacrylate and benzyl methacrylate on the polymer tacticity through a modified microemulsion polymerization procedure. They found that the syndiotacticity of the product decreased when the polymerization was carried out at a temperature far above the Tg of the resulting polymer and that the tacticity of polymer was affected by the monomer structure, a monomer with the bulkier alkyl side group would liable to result in a polymer with richer syndiotacticity.

# Experimental

The monomers (Aldrich, > 99%) of MMA, ETA, BMA, HMA and 2-EHMA were purified by distillation under reduced pressure. The surfactant SDS purchased from Hycel (Guadalajara, Mex. > 99%) and the initiator KPS purchased Aldrich (> 98%) were used as received. The water used in the experiments was bi-distilled grade. It was used Argon (Infra<sup>TM</sup> of ultra high purity) to remove the oxygen of the system.

The one-phase o/w microemulsions at 25 °C were determined visually by titrating aqueous micellar solutions of SDS with the monomers. Batch polymerizations were made using a spherical glass reactor (250 mL) with two inlets and a port at the bottom for sampling. Magnetic stirring was used in all reactions. A condenser with reflux was mounted in one neck of reactor. The compositions used in polymerizations are shown in Table 1. In all cases, the water/surfactant ratio were 94/6 wt./wt. Water, SDS and KPS were charged to the reactor and bubbled with argon (ultra high purity from Infra ®) by one hour. After that, the temperature was raised to 60 °C by passing water from a bath through the jacket of reactor. Monomer was added using a syringe with needle to start polymerization. Samples were taken at different times to determine conversions by gravimetry (mass balances) and particle sizes (Dynamic Light Scattering, Nano S-90, Malvern).

Run	Water (g)	SDS (g)	KPS (g)	Monomer (g)
MMA (2.5%)	137.475	8.775	0.0375	3.75
EMA (2.5%)	137.475	8.775	0.0375	3.75
BMA (2.5%)	137.475	8.775	0.0375	3.75
HMA (2.5%)	137.475	8.775	0.0375	3.75
2-EHMA (2.5%)	137.475	8.775	0.0375	3.75
MMA (3.5%)	136.065	8.685	0.0375	5.25
EMA (3.5%)	136.065	8.685	0.0375	5.25
BMA (3.5%)	136.065	8.685	0.0375	5.25
HMA (3.5%)	136.065	8.685	0.0375	5.25
2-EHMA (3.5%)	136.065	8.685	0.0375	5.25

Table 1. Recipes uses in the polymerizations at 60 °C.

# **Results and Discussions**

Before polymerization starts, microemulsion system consists of monomer dissolved in the aqueous phase and monomer inside the microemulsion droplets. When polymerization is initiated, some of the microemulsion droplets become particles by capturing radicals propagating in the aqueous phase (micellar nucleation). Particle formation also can occurs by homogeneous nucleation when radicals in the aqueous phase grow until a critical size is reached, precipitating from the aqueous phase; these precipitated radicals can absorb surfactant and self-stabilize, producing a stable polymer particle. High reaction rates (Rp) were observed in all runs. Figure 1 shows the effects of

#### MACROMEX 2011

monomer type (a) 2.5 % of monomer content, (b) 3.5% of monomer content. For 3.5 wt. % of monomer concentration, at the beginning of reaction there is no significant difference in the polymerization rate, however, at high conversions, the order of polymerization rate were  $Rp_{EMA} > Rp_{BMA} > Rp_{HMA} > Rp_{2-EHMA} > Rp_{MMA}$ , whereas for 2.5 wt. % of monomer concentration, the polymerization rate were  $Rp_{BMA} > Rp_{HMA} > Rp_{2-EHMA} > Rp_{2-EHMA} > Rp_{2-EHMA} > Rp_{2-EHMA}$ . Two periods of polymerization were observed, which is typical in microemulsion polymerization.



Figure 1. Conversion vs. time of the different runs (a) 2.5% of monomer content (b) 3.5% of monomer content.

Table 2 shows the final average particle diameter (Dp) for the different runs. It can be seen that Dp increases the alkyl group of the monomer increases and with the monomer concentration as a direct consequence of the hidrophobicity of monomers.

In Figure 2 the particle size distributions (PSD) at different monomer type and concentrations are shown. Narrow PSD's were obtained (Polydispersity Index in sizes, PDI, in Table 2) for all runs.



Figure 2. Particle size distribution of final latexes obtained for the different runs and different monomer concentrations.

	2.50%		3.50%	
Monomer	Dp, nm	PDI	Dp, nm	PDIS
MMA	42.35	1.3443	46.16	1.2984
EMA	50.09	1.1762	53.69	1.3214
BMA	55.97	1.1724	59.94	1.3278
HMA	63.96	1.255	65.32	1.3563
2-EHM	58.88	1.256	64.43	1.3975

Table 2. Average particle diameters and polydispersity in sizes (PDI) of final latexes.

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### RHEOLOGICAL CHARACTERIZATION OF THE GEL POINT IN POLYMER-MODIFIED ASPHALTS

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Asphalts are materials widely used in paved roads due to good adhesion with mineral solids, low cost, and adequate viscoelastic properties [1–3]. With the purpose to improve the mechanical and thermal properties of asphalt, a variety of polymers are used, among them functionalized polymers. In particular, styrene-b-(ethylene-1-butene)-b-styrene "SEBS" copolymers functionalized with maleic anhydride (MAH), (SEBS-g-MAH) have been used as compatibilizers of immiscible polymer blends.

The samples of modified asphalts were obtained after high-temperature storage tests using asphalt (with 80/20 wt % maltene/asphaltene composition) mixed with SEBS polymers grafted with specific amounts of MAH (SEBS-MAH24, SEBS-MAH34, SEBS-MAH54, and SEBS-MAH74). The polymer content in the asphalt is 4 wt %. The properties of modifier polymers are shown elsewhere. SEBSMAH24, 34, 54 and 74 means 4 wt. % polymer and 2, 3, 5 and 7 wt. % MAH.

The rheological properties of gelling systems were studied as a function of the degree of crosslinking. It was found that stable mixtures can be obtained if the MAH content is maintained below 5 wt %, while higher.

MAH content leads to gel formation during the curing process. The blends asphalt/SEBS04 and asphalt/SEBS-MAH24 do not contain gel, since these blends are in the prepolymer stage, while that asphalt/SEBS-MAH34 and asphalt/SEBS-MAH54 are in the sol–gel transition zone. In particular, asphalt/SEBS-MAH54 is the blend where critical gels are generated.

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# IMPROVED DISPERSION OF CARBON NANOTUBES IN A POLYPROPYLENE MATRIX THROUGH ULTRASOUND ASSISTED MELT MIXING

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#### Abstract

Preparation of masterbatches of multiwalled carbon nanotubes (MWCNTs) in isotactic polypropylene (iPP) by melt mixing assisted by ultrasound and their dilutions in iPP were studied. Two different molecular weights (namely low and high) of iPP were used to prepare masterbatches with 20 wt/wt % MWCNTs. In order to evaluate the masterbatches' feasibility as a MWCNTs carrier to facilitate dispersion in nanocomposites, these were diluted in a medium molecular weight iPP matrix to 1, 2, and 6 wt/wt %. Nanocomposites with 1% weight of MWCNTs showed interesting electrical, mechanical, and thermal behavior. Values of volume conductivity reached 5 x  $10^{-5}$  S/cm, Young's modulus increase in 50% and crystallization temperature increased up to 9°C from neat polymer. In general, the use of low molecular weight masterbatches shows an improved dispersion compared to medium molecular weight, even at low MWCNTs' concentrations. We conclude that ultrasound energy leads to a good dispersion of large quantities of MWCNTs in iPP avoiding the use of high shear strain that could damage the MWCNTs

#### Introduction

Carbon nanotubes (CNTs), discovered in 1991 by Iijima[1], are one of the most studied nanoparticles in the last 10 years since they have potential application in electronics, medical, energy storage, among others, due to their excellent electrical<sup>[2]</sup>, mechanical<sup>[3, 4]</sup> and thermal<sup>[5]</sup> properties. Particularly, carbon nanotubes can be introduced polymers forming nanocomposites for use in a wide range of industries such as electronics, aerospace, medical, packaging, sports, electrochemical sensors, etc. Obtaining outstanding properties of nanocomposites depend on three main factors: nanoparticle functionality, interaction between fillers and matrix, and an adecuate dispersion of nanoparticles on the polymer matrix. Nevertheless, CNTs tend to agglomerate being this one of the major challenges in preparing CNTs/polymer nanocomposites since a full dispersion is hard to obtain. Methods such as in-situ polymerization, solution mixing[6], melt mixing, electrospun[7] have been used with certain success and limitations. Melt mixing presents some advantages besides the other processes for industrial production of nanocomposites, such as low production cost, due to the use of conventional polymer processing equipment, and it is environmental friendly since no solvents are used. One disadvantage for this process is the use of high strain shear to break apart nanotubes agglomerates that can also cause break CNTs and can degradate the polymer. To overcome this problem, Isayev et al[8]reported the preparation of polyetherimide/multiwall carbon nanotubes (MWCNTs) nanocomposite by melt mixing using an ultrasound tip to improve filler dispersion, obtaining an increase on properties values with low concentrations of nanotubes (1-10% wt/wt).

In this work we present an improved method to preparate a nanocomposite with isotactic polypropylene and multiwall carbon nanotubes (iPP/MWCNTs) with low concentration (1, 2 and 6% w/w) through the dilution of a masterbatch (20% wt/wt MWCNT) preparated by melt mixing assisted by ultrasound.



Figure 1 Esquematic diagram for extrusion system adapted with ultrasound

## Experimental

## Materials.

Multiwall carbon nanotubes were provided by Chendu Alfa Nanotech Co., Ltd., China, with external diameter of 30-50 nm, average length of 5-30  $\mu$ m, purity >90%, and surface area >110 m<sup>2</sup>/g and were used as received. Two molecular weight isotactic polypropylene provided by Aldrich Sigma were used, 12,000 and 190,000 g/gmol named iPP-12K and iPP-190K respectively.

### Masterbatch preparation.

Materials were premixed to a concentration of 20% wt/wt MWCNTs in an internal mixer Brabender Plasticorder DR 2071, with 50 rpm and temperatures of 170°C and 180°C for iPP-12K and iPP-190K respectively. Masterbatches were then prepared by melt mixing in a Dynisco lab extruder adapted with an ultrasound chamber (Figure 1). Power values of 0, 150, 190, 225, and 260 watts were applied using a Cole Palmer ultrasonic homogenizer (750W).

**Nanocomposites preparation.** Based on characterization analysis we selected 3 masterbatches for each molecular weight: processed with 0, 190 and 225 watts ultrasonic power, and diluted it to 1, 2 and 6% wt/wt MWCNTs in an iPP-190K matrix. Nanocomposites were prepared in the Dynisco lab extruder without ultrasound.

**Characterization.** Nanocomposites fracture behavior was evaluated in a JEOL JSM-7041F scanning electronic microscopy by cryogenic fracture. Thermal properties were analyzed by differential scanning calorimetry in a TA Instruments 2920 modulated DSC, using a 10 °C/min heating ramp in  $N_2$  atmosphere. Thermal gravimetric analysis (TGA) were performed in a TA Instruments TGA Q 500 with 10 °C/min heating ramp in a  $N_2$  atmosphere from 30 to 600°C, and from 600 to 800°C a  $O_2$  atmosphere with 20°C/min ramp. Volume electric conductivity were calculated from resistance values obtained through 4 points Cabot method at room temperature from pill shape samples using a circuit equipped with a Zúrich DS304M power source, a Simpson 461-2 multimeter and a Steren Mul-600 RS232C voltimeter. Pill samples were prepared in a Mettler Toledo FP82HT hot plate programmed with a 10°C/min heating and cooling ramp. Strain/stress were performed at room temperature in a Instron 430 testing machine using a speed of 0.1 in/min. Probes were prepared from 1 mm thickness plates in dog bone shape according DIN 53504. Five specimens for each sample were tested for reproducibility..

### **Results and Discussion**

**Masterbatches.** The crystallization temperature of MBs increases 18°C and 16°C, for MBs iPP-12K and iPP-190K respectively compared to neat polymer. This thermal behavior suggests that



Figure 2. Masterbatches electrical conductivity behavior

**Figure 3.** Termograph of DSC for crystallization behavior of nanocomposites with MBs iPP-12K

carbon nanotubes act as nucleation agents[9]. Besides, masterbatches showed higher degradation temperature, increasing up to 70°C for iPP-12K and 35°C for iPP-190K, probably due to the fact that CNTs can act as a gas barrier reducing degradation rate[10]. On the other hand, electrical conductivity showed by MBs is in the range of semiconductors. The use of different ultrasound power allowed to obtained grades of deagglomeration and dispersion of MWCNTs, reflected in higher electrical conductivity values. In Figure 2 we can identify three zones for masterbatches electrical behavior: in first zone, electrical conductivity is the result of a high MWCNT concentration without significant ultrasound effect. In medium zone we observe an important increase in conductivity that indicates an ultrasound positive effect on CNTs dispersion for both iPPs. Zone 3 shows an opposite effect for each molecular weight masterbatches. In this, electrical conductivity values for MB iPP-12K increased while they diminished in the case of MB iPP-190K. The results suggest that ultrasound energy affects both CNTs agglomerates and polymers chains simultaneously, but in different ways. We speculate that ultrasound has a bigger effect on agglomerates with low molecular weight polymers, whereas in the case of higher molecular weight polymers, the energy is dissipated in both phases, agglomerates and polymer chains, leading to a low deagglomeration effect.

**Nanocomposites.** In order to evaluate masterbatches feasibility to use as a MWCNT carrier, they were diluted in an iPP-190K matrix and their morphology and properties were analyzed as follows. Use of different powers of ultrasound in MBs preparation showed a significant effect on CNTs dispersion and was reflected in improved properties. Crystallization temperature for all nanocomposites prepared with both molecular weights MBs increased in comparison to neat polymer even at 1% wt/wt MWCNTs concentration (Figure 3). Ultrasound effect was larger for low molecular weight MBs at low concentrations, indicating a higher interaction between the phases. SEM images show strong iPP-MWCNTs interaction. For example, for nanocomposites with 1 % wt/wt MWCNTs from MB iPP-12K (190W), it shown that polymer is attached to the nanotube surface, while in other cases holes (yellow arrows) due to fractures stress are observed (Figure 4). Polymer nanocomposites with 2 % wt/wt MWCNTs is used for both low and high molecular weight masterbatches.





**Figure 5.** Electrical conductivity behavior for nanocomposites with MBs iPP-12K

Electrical conductivity of iPP/MWCNTs nanocomposites are in the range of semiconductors, contrary to the neat iPP which is an insulating material. Even at low MWCNTs content the electrical conductivity is in the range of 10<sup>-6</sup> S/cm when ultrasonic waves were applied at the MBs preparation, however the electrical conductivity was below 10<sup>-8</sup> S/cm of when no ultrasound was used. Besides, incorporation of MWCNTs from low molecular weight MBs increases the Young modulus from 385 MPa for the neat iPP to 570 MPa with 1 % wt/wt MWCNT (more than 40 % increase). This effect is less pronounced using high molecular weight MBs, since the maximum modulus reached was 560 MPa. The best performance of low molecular weight MB can be associated to a lower polymer chains size that leads to a higher ultrasound energy transferred to CNTs agglomerates producing a better disentangling and hence a better dispersion in nanocomposites preparation.

#### Conclusions

In this study we propose an improve method for preparation of nanocomposites by melt mixing using high concentration masterbatches elaborated by melt mixing assisted with ultrasound. Effects of MWCNTs incorporation on a polymer matrix were evaluated. Thermal and electrical properties were improved even at low nanotubes concentration. 1 and 2% wt/wt MWCNTs showed a significant increase in properties. Ultrasound power showed different effects according to the molecular weight of iPP. For low molecular weight masterbatches high ultrasound energy (225 W) presented better effect, while for high molecular weight masterbatches medium ultrasound energy (190 W) showed the better results.

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# SYNTHESIS OF POLYESTER RESIN FROM ROSIN INDUSTRIAL WASTE AND DEGRADED PET

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#### Abstract

Synthesis of new polymers from waste materials has become a growing area with the goal set to be the diminishing of environmental pollutant materials. For this reason, in this work, the synthesis of a polyester resin derived from rosin and oligomers from the degradation of recycled PET is presented. The rosin was characterized by FTIR, TGA and DSC. The esterification reaction between rosin and oligomers was carried on in a 1:1 ratio, using  $Zn(OAc)_2 \cdot 2H_2O$  as a catalyst (16.8% in weight in relation to rosin), in the absence of solvents. The polyester resin was characterized by FTIR, GPC, DSC, TGA and hydroxyl index; the results suggest it is a thermally stable resin with a low molecular weight (864 g/mol), with a potencial application into the formulation of varnishes.

#### Introduction

One of the principal products from forestry sector is the pine resin, which is an oleoresin constituted by a volatile fraction denominated turpentine, in where are mainly compounds as  $\alpha$ -pinene,  $\beta$ -pinene, silvestreno and dipentene, and a non-volatile fraction denominated rosin, which is chiefly composed of rosin acids<sup>1</sup>. One of the main characteristics of rosin acids is the presence of two chemically active centers: the double bonds and the carboxyl group, thus they can be modified by reactions of addition or esterification. Within the modifications realized to rosin are of interest those carried out by esterification using mono or polyols, because the esters obtained presented resistance to the water, acids or alkalis, which is attributed to the steric hindrance that present the ester bond formed<sup>2</sup>. In recent years is reported the obtaining of rosin esters derivatives of polyols as ethylene glycol (EG), diethylene glycol (DEG), polyethylene glycol(PEG), etc.<sup>3-7</sup>, though, others molecules that have similar structure properties to these polyols are the poly(ethylene terephthalate)<sup>8</sup> oligomers (PET), so that result of interest their apply in the formation of new compounds derivatives from rosin.

In the present work was carried out the esterification of rosin with oligomers from PET degraded in order to obtain a polyester resin with potential application inside the formulation of interior coatings, lacquers o varnishes.

### Experimental

### Isolation and abietic acid treatment

It was added 1.6 mL of HCl concentrated in dissolution of 10 g of rosin contained in 29 mL of ethanol, the mixture was heated to reflux temperature for 2.5 hours under nitrogen atmosphere. Later, the dissolvent of mixture reaction was eliminated in a rotator evaporator, the residue was dissolved in 40 mL of ethylic ether and was realized three extractions with 10 mL of water each one. Then ether extract was dried with CaCl2 and the dissolvent was eliminated for rotary evaporation.

The extract obtained was dissolved in 15 mL of acetone, heated and was added 4.8 g of dipentylamine, finally was cooled in an ice bath until precipitation. The amine salt was purified

three times by recrystalization using 20 mL of acetone. With the purpose to obtain the abietic acid from amine salt, it was prepared a dissolution of 3.5 g of salt in 24 mL of ethanol 95%, which later was cooled to 5°C, it was added 0.95 g of acetic acid concentrated.

To the reaction mixture obtained was added 25 mL ethylic ether and were realized three extractions using 10 mL of water (per extraction).

Finally, the ether extract was left to slow evaporation until the formation of triangular crystals of light yellow color<sup>4,5</sup>.

#### **Chemically degradation of PET**

It was prepared a mixture with 40 g of PET pellets, 80 mL of diethylene glycol, 0.2 g of zinc stearate and 0.2 g stannous chloride, the mixture was heated to  $210^{\circ}$ C for 2h with constant stirred. Later, it was added 10 mL of hot water and realized a quenching with the purpose to precipitate the oligomers obtained. The oligomers were separated of the reaction mixture per decantation and finally were dried in the stove to  $110^{\circ}$ C for 24 hours<sup>9</sup>.

#### Abietic acid esterification

A sample of 1.10 g of rosin was heated to  $140^{\circ}$ C on a glycerin bath, then was added 0.53 g of PET oligomers and zinc acetate (16.8 % in weight in relation to rosin) as catalyst. The reaction was carried out for five hours to  $140^{\circ}$ C. One time finalized the reaction, was left cool and added 30 mL of ethylic ether to separate the resin from the mixture reaction. Finally the resin obtained was filtered to vacuum and washed with 15 mL of ether ethylic. In the Figure 1 is illustrated the reaction scheme.

Scheme of synthesis of resin for the reaction the abietic acid with degraded PET. It determined the hydroxyl and acid index of the PET oligomers and polyester resin according to ASTM D1957-86 and ASTM D4662-87, as well as the Pharmacopoeia of the United Mexican States (2008) AMS 0491.

#### **Results and Discussion Isolation of abietic acid**

The abietic acid isolated from rosin was obtained as triangular crystals of light yellow color with melting point of 162.6°C, which corresponds to the reported in literature<sup>5,10</sup>. In the Figure 2 is show its UV-Vis spectrum, where is observed a maxim absorbance peak to a wave length of 241 nm characteristic of abietic acid11.

1.



Figure 2. UV-Vis spectrum of abietic acid.

In the Figure 3 is show the FTIR spectrum of abietic acid isolated, in which is displayed the bands assignable to the stretching C=O (1690 cm-1), O-H (3421, 950 cm-1) corresponding to carboxyl group, while the intensified of stretching to 951 cm-1 and the attenuation of band to 3421 cm-1 (both corresponding to -OH group) suggest that resin acid was found as dimers because of the formation of hydrogen bond intramolecular.



#### Characterization of the degraded PET oligomers

The PET oligomers were characterized by gel permeation chromatography (GPC), hydroxyl index, FTIR and DSC. In Table 1 the results are displayed, the molecular weight indicated that PET degradation was carried out until formation of dimer BHET.

Table 1. Physico-chemical properties of the degraded PET oligomers.						
Sample	Mn	Mw	D	Hydroxyl index		
-				(mg of KOH/g)		
O-PET	435	638	1.46	282.49		

The FTIR spectrum corresponding to the PET oligomers show the characteristic bands of a polyester resin: stretching of C=O, C-O y OH. The DSC thermogram of the residue showed that have Tg of 48°C y Tf of 145°C, by TGA was determinated that it experience a loss in weight in two ranges of temperature:  $65.7^{\circ}$ C-184.3°C y 184.3°C-300°C, giving a totally weight loss of

23.31% which is attributed to the degradation of oligomers of low molecular weight and/or volatile impurities.

#### **Esterification reaction**

The reaction product between the abietic acid and the degraded PET oligomers was obtained as light yellow dust, with melting point of  $142.5^{\circ}$ C. In the Figure 4 is show the IR spectrum, is observed the stretching of C=O y C-O characteristics of the esters, as well as the disappearance of the band corresponding to –OH group present in the oligomers of PET, that suggest that the esterification was carried out and therefore the obtain of resin polyester.



Figure 4. FT-IR spectrum of polyester resin.

In the Table 2 is displayed the values of Mn, Mw and polydispersity index, Mw value of the product show an increase of 226 units in relation to Mw of oligomer, which suggest that esterification was carried out on one of the terminal hydroxyl groups of chain PET oligomers, that is to say, in a relation 1:1, as well as this was corroborated by means of the diminution of approximately 50% in the index of hydroxyl of resin polyester in comparison to which displayed the oligomers before reacting with abietic acid.

Table 2. Physico-chemical properties of polyester resin.						
Sample	Mn	Mw	D	Hydroxyl	index	
-				(mg of KOF	ł∕g)	
Polyester resin						
	486	864	1.77	157.90		

### Conclusions

As a result of esterification reaction between abietic acid extracted of rosin and the residue obtained from chemically degraded PET, is obtain an ester with molecular weight 864 g/mol, this value indicates that the residue from the degradation of PET was chiefly formed by BHET dimer before reaction, which was esterified with abietic acid occupying the functional groups OH, that is conclude due to the decrease of hydroxyl index.

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# SYNTHESIS OF RUBBER MODIFIED POLYSTYRNE IN A TWIN-SCREW EXTRUDER TYPE REACTOR

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In recent years, interest has been growing in the use of extruders as polymerization reactors [1]. Extruders have been used to resolve heat and mass transfer problems that arise from dramatic viscosity increase in batch mass polymerization processes [2]. On the other hand, styrene is an inexpensive, reactive monomer employed for the production of general-use polymer resins. However, their widespread application is limited by the brittleness of polystyrene. In order to overcome these limitations, such polymer resins are toughened with rubber by a process known as suspension and mass polymerization, and it is commonly used to produce high impact polystyrene (HIPS).

Considering that efficient mass polymerization of styrenic resins in extruders has been reported [3], in this communication we report the synthesis of HIPS in a twin-screw extruder. Several rubbers were tested, including polybutadiene and styrene/butadiene (SBR) with different polystyrene (PS) composition. The HIPS produced were characterized by gel permeation chromatography (GPC), transmission electron microscopy (TEM) and mechanical properties were determined. In all HIPS obtained, the morphological structure contained polystyrene occlusions and the impact strength exhibited values between 1 and 3.5 ft-lbf/in. The mechanical properties are attributed to variations in the particle size as a result of the change in PS composition in the rubber used.

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# SYNTHESIS AND SELF-ASSEMBLY IN THIN FILMS OF BLOCK COPOLYMERS OF POLYSTYRENE-b-POLYDIETHYLAMINOETHYL-METHACRYLATE (PST-b-PDEAEM).

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#### 1. Abstract

Linear AB block copolymers where A and B are immiscible, assemble in the solid state into ordered complex morphologies. The type and size of the morphology can be controlled by the composition and molecular weight of the block copolymer. Most of these polymers with molecular weights of 20 to 200 K g.mol<sup>-1</sup>, show domain sizes from 10 to 100 nm, representing interesting new nanomaterials. In this contribution we report the preparation of diblock copolymers of polystyrene (PSt) a hydrophobic polymer, as first block; and polydiethylaminoethylmethacrylate (PDEAEM) a ionizable polymer, as second block. All block copolymers were synthesized controlling their size and composition by means of reversible addition-fragmentation chain transfer (RAFT) polymerization. As RAFT agent 4-cyano-4-(dodecylsulfanylthiocarbonyl) pentanoic acid was used. Block copolymers with different composition of polystyrene (90 % and 60%), according to the theoretical phase diagram reported by Matsen were prepared aiming different morphologies like packed spheres and lamellar sheets. Thin films were obtained by means of Spin-Coating over glass slides, observing good segregation of the domains. Different annealing methods were tested to improve the regularity of nano-domains formed by self-assembly in the solid state, as studied by AFM micrographs.

#### 2. Introduction

Block copolymers have received great attention for the past 40 years but only within the past decade have they been seriously considered for nanotechnological applications [1]. Their applicability to nanotechnology stems from the scale of the microdomains and the convenient tunability of size, shape, and periodicity afforded by changing their molecular parameters. The self-assembly property of block copolymers has lead to the design of a number of highly sophisticated nanostructured soft materials which today open a new frontier in material science having implication in many fields such as: data storage media, separation membranes, high surface area catalyst supports, biosensors, photovoltaic cells, photonic crystals , drug delivery and many others where ordered microphase separation at the nanoscale is a crucial factor [2] [3].

Matsen and Schick mean-field theory [4] showed that the phase behavior in the case of a diblock copolymer is determined by two parameters, namely,  $\chi N$  and f, where  $\chi$  is the Flory-Huggins segment-segment interaction parameter, N is the degree of polymerization, and f is the block copolymer composition. The product  $\chi N$  determines the degree of segregation of the blocks. Leibler [5] showed that For  $\chi N < 10.5$  the block copolymers do not show microphase separation and the entropy of mixing dominates the free energy of the blend. Close to the ODT the system is in the so called weak segregation limit where the interface between the domains is somehow diffuse. In contrast, in the strong segregation limit ( $\chi N >> 10.5$ ) the narrow interfaces will separate well-developed almost pure micro domains. For diblock copolymers, a lamellar (lam) phase is observed for symmetric diblocks (f = 0.5), where as more asymmetric diblocks form hexagonal-packed cylinder (hex) or body-centered cubic (bcc) spherical structures. A complex bicontinuous cubic gyroid (gyr) (space group Ia-3d) phase has also been identified for block copolymers between the lam and hex phases near the ODT, and a hexagonal-perforated layer (HPL) phase has been found to be metastable in this region [4,5].

The last 20 years has been witness to unprecedented advances in controlled polymer synthesis.

This has been due, in part, to the discovery and development of controlled free radical polymerization (CRP) techniques [6]. Among the above techniques, RAFT is a versatile method capable of inducing living behavior for various monomers via a range of initiation methods and varying reaction temperatures [7]. RAFT also enables the formation of a variety of molecular architectures such as block copolymers, star shaped molecules and comb structures [8].

### 3. Experimental

#### 3.1 Polymerizations (Macro-CTA's)

polymerizations All were performed in ampoules. all In 4-cvano-4cases. (dodecylsulfanylthiocarbony) pentanoic acid and 2,2'-Azobis(isobutyronitrile) (AIBN) were used as the chain transfer agent (CTA) and initiator, respectively. The monomers, CTA and initiator were dissolved in 1,4-dioxane. Solutions were degassed by three freeze-pump-thaw cycles. After degassing, the ampoules were flame-sealed under vacuum and heated in an oil bath at 70 °C. The polymerizations were terminated by rapid cooling and freezing. The homopolymers obtained, also named macro-CTA's since they include the CTA-moiety, were purified by repeated precipitations. Products were dried in vacuum.

### 3.2 Block Copolymerizations

Well characterized homopolymers synthesized in the first step were used as macro-CTA's. The maco-CTA was dissolved in 1,4-dioxane (10 ml) before adding the second monomer in different amounts aiming different compositions, and the initiator. The copolymerization procedure was the same as for polymerization.

#### 3.3 Characterization methods

The homopolymers and block copolymers were characterized by gel permeation chromathography(GPC), nuclear magnetic resonance (RMN), differential scanning calorimetry (DSC) and thermogravimetry (TGA).

### 3.4 Thin Film preparation

Thin films were prepared by spin coating. An excess amount of polymer solution is placed on the glass substrate. The substrate is then rotated at high speed in order to spread the fluid by centrifugal force. Rotation is continued for some time, with fluid being spun off the edges of the substrate, until the desired film thickness is achieved. The solvent is usually volatile, providing for its simultaneous evaporation. Polymer thin films were prepared by spin coating from benzene and toluene solutions, containing 1 % (w/w) polymer onto glass plates and dried overnight at room temperature.

### 4. Results and Discussion

For the block copolymer preparation two strategies were tested: making first a PSt homopolymer and using it as macro-CTA to grow in the second step polyDEAEM; and making first a PDEAEM homopolymer and using it as macro-CTA to grow in the second step polySt. The best strategy was to start with PSt homopolymers and using them as macro-CTA. This is due to the fact that a PSt growing radical is more stable than a PDEAEM growing radical. The formation of PSt homopolymer not attached to the block copolymer during block copolymer formation is more pronounced when a macro-CTA of PDEAEM was used. The choice of monomer order by copolymerization when aiming block copolymers by RAFT was recently documented [9]. Table 1 shows the characteristics of two block copolymers synthesized with different compositions, obtaining molecular weights of 58,430 and 88,240 g/mol, with low polydispersities. Taking the composition of the block copolymers as base, it is expected that in thermodynamic equilibrium they will tend to form spheres and lamellae (Table 1).

		· · · · · · · · · · · · · · · · · · ·				
Diblock	Macro-CTA	Mn	PDI	f	Tg	Tg
	$(M_n g/Mol)^a$	$(g/Mol)^a$	$(M_w/M_n)^a$	PSt	PSt	PDEAEM
		0			(°C)	(°C)
PSt-b-PDEAEMA	PSt (54,720)	58,430	1.15	0.10	101	-9
PSt-b-PDEAEMA	PSt (53,500)	88,240	1.20	0.60	95	-5
9						

Table 1. Molecular characteristics of diblock copolymers.

<sup>a</sup> From GPC

<sup>b</sup> From RMN

Thermal analysis of the block copolymers are shown as compared to the respective homopolymers by DSC (Fig 1 A). Thermograms show the glass transition temperature of the macro-CTA of PSt (101 °C) and a macro-CTA of PDEAEMA (-9 °C); the block copolymer shows both glass transitions as expected for not miscible blocks. In Figure 1B the thermogravimetric analysis shows the decomposition temperature of the two blocks synthesized, which shows that both materials begins to decompose after 300 °C. These thermogravimetric analysis were performed with the aim of providing post-treatment to thin films of diblock copolymers, to help achieve the equilibrium thermodynamics of polymer molecules.



Figure 1. A) DSC of copolymer diblock of  $PSt_{90}$ -b-PDEAEM<sub>10</sub>,macro-CTA(PSt) and of block and the second block of the copolymer (PDEAEM). B) TGA of the two diblock copolymers  $PSt_{90}$ -b-PDEAEM<sub>10</sub> and  $PSt_{60}$ -b-PDEAEM<sub>40</sub>.

Figure 2 shows images of films prepared by spin-coating, using copolymers with different composition: spheres ( $f_{PSt} = 0.10$ ) (Figure 1A), lamellae ( $f_{PSt} = 0.60$ ) (Figure 1B). These films were prepared using the same conditions for both copolymers: concentration (1%), speed (2000 rpm), solvent (benzene), showing good segregation to the nanostructure type expected for each copolymer.



Figure 2. AFM images obtained from thin films prepared by spin-coating, using benzene as solvent, concentration 1% and speed of 2000 rpm.

Figure 3 shows the images of the thin film prepared by spin coating of the copolymer ( $PSt_{60}$ -*b*-PDEAEM<sub>40</sub>) (Figure 3A) using toluene as solvent at 5000 rpm; and after heat treatment with toluene solvent vapor for 90 h (Figure 3B). Good segregation is observed, however the lamellae structure is not easily recognized.



Figure 3. AFM images obtained from thin films ( $PSt_{60}$ -b-PDEAEM<sub>40</sub>) prepared by spin-coating, using toluene as solvent, concentration 1% and speed of 5000 rpm. A) Obtained from the spin coatig. B) After treatment with toluene vapor for 90 h.

Figure 4 shows micrographs of a film prepared using a benzene solution (concentration of 1%) of the block copolymer ( $PSt_{90}$ -*b*-PDEAEM<sub>10</sub>) and a rotation speed of 5000 rpm (Figure 4A). After heat treatment at 120 °C for 130 h, the formation of rectangles and not well-defined clusters is observed (Figure 4B).



Figure 4. AFM images obtained from thin films ( $PSt_{90}$ -b-PDEAEM<sub>10</sub>) prepared by spin-coating, using benzene as solvent, concentration 1% and speed of 5000 rpm. A) After spin coating. B) after a heat treatment at 120 °C for 130 h.

#### Conclusions

Two diblock copolymers with different compositions were synthesized using the RAFT technique:  $PSt_{90}$ -b-PDEAEM<sub>10</sub> and  $PSt_{60}$ -b-PDEAEM<sub>40</sub>. It was important to start with PSt macro-CTA's to achieve the desired block copolymers. The two block copolymers obtained showed the expected microseparation directly by spin coating over glass slides, using solutions in benzene and in toluene, both with concentration of 1%. Different treatments were applied to improve the microseparation. The mobility of the chains of the block copolymers was attained by steam of toluene, benzene and by heat treatment. Toluene vapor improved segregation keeping the same pattern and in the other cases, agglomeration of domains was shown.

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#### STRUCTURE AND PROPERTIES OF CHITOSAN-SILVER NANOPARTICLES NANOCOMPOSITES

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Chitosan/silver nanoparticle (CS/AgnP's) nanocomposites have wide range of applications in materials science, biomedical field, construction of biosensor, food industry, etc. The properties of the nanocomposites dependent not only on the type of nanoparticles but also on their concentration, distribution, methods of preparation, interaction with chitosan matrix. Due to the above, the aim of this work is to synthesize CS/AgnP's films using different methods and to investigate the influence of the nanoparticles concentration and its dimension on structure, electrical and dielectical properties.

Three different types of CS/AgnP's films (with thickness 30 mkm) were prepared using a solventcasting method. 1) AgnP's powder was dissolved in chitosan-acetic acid solution by sonication method. 2) Reducing of silver nitrate salt with ascorbic acid as reducing agent and sodium dodecyl sulfate as stabilizer in the chitosan solution. 3) Reducing of silver nitrate salt with nontoxic ascorbic acid as reducing agent and sodium citrate as stabilizer in the chitosan solution. The average size of particles were determined by Dynamic Light Scattering which shows that the average size of the nanoparicles were 25 nm, 20 nm and 50 nm respectively. Uv-Vis spectra for the nanocomposite films showed a band between 400-450 nm, which suggests the formation of Ag nanoparticles in the chitosan matrix. FT-IR spectrum reveals that the band 3300-3500 cm<sup>-1</sup> is characteristic of the N-H bending vibrations. The significant decrease of transmittance in this band region indicates that the N-H vibration was affected by the attachment of AgnP's. XPS spectroscopy indicated the presence in the films both metallic silver and silver ions.

Two relaxation processes have been observed in all films: 1) in the wet films (with water content between 1-11 wt % (TGA measurements) the alpha-relaxation associated with the glass-rubber transition; 2) the second relaxation was observed in the temperature range  $90-160^{\circ}$ C C has been identified as the sigma-relaxation which is often associated with the hopping motion of ions in the disordered structure of the biomaterial. These relaxation processes dependent on the method of preparation and concentration of AgnP's. Based upon the above results, a plausible mechanism of interaction between AgnP's and chitosan matrix has been proposed.

# EFFECT OF SYNTHESIS VARIABLES ON THE FLUORESCENCE OF CDSE QUANTUM DOTS - POLYSTYRENE LATEXES

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#### Abstract

The process of miniemulsion polymerization permits the encapsulation of quantum particles into a polymer matrix providing them of chemical stability without affecting their luminescent properties. In this work, the synthesis process was conducted varying levels of surfactant, initiator and CdSe QDs. A microscopy study on the composite latexes and later a statistical analysis indicated that the increment in surfactant concentration produced a decrease in the polymer particle size, which increased in turn the rate of polymerization and percentage conversion. The obtained latexes were stable and showed fluorescence by excitation with UV light. The spectrofluorometry studies indicated that in composite latexes the fluorescence was a function of polymer particle size and the amount of encapsulated dots per polymer particle.

#### Introduction

Cadmium selenide quantum dots (CdSe QDs) are semiconductor nanocrystals from II-VI group. Due to their zero-dimensional quantum confinement and their size (1-10nm), they own extensive absorption spectra with narrow and symmetric emission bands when they are excited by a single light source [1,2]. The incorporation of semiconducting nanocrystals into a polymer matrix increase QDs photostability and improves optical characteristics [3-5], producing a solid material with specific optical properties and offering new perspectives to studies and applications [6-8].

The miniemulsion polymerization process implicates the formation of monomer droplets uniformly dispersed and stable within a continuous phase, which become the reactors to generate latex polymer with characteristics determined by variables in their kinetics and synthesis [8-9]. This synthetic technique allows the dispersion of the QDs in the polymer particles due to phase affinity between the monomer and them, which protects QDs structure and emission characteristics [3,5]. By changing the synthesis variables it is possible to modifying the polymer particle size, which in turn, produces changes in both the QDs/polymer particle ratio and the fluorescent emission intensity.

The purpose of this study was to determine the effect of miniemulsion variables on the fluorescence of CdSe QDs/ polystyrene latexes. It was considered that variations in the surfactant and initiator concentrations reflect changes in the polymer particle size and rate of polymerization. It is expected that by controlling these changes it could be possible the design of fluorescent polymer composites with tailored functionality.

# Experimental

### Miniemulsion polymerization

Miniemulsion polymerization process was achieved using cetyltrimethylammonium bromide (CTAB) as the surfactant, at concentration levels of 1.3x10-3M, 3.2x10-3M and 5.4x10-3M. The initiator 2,2-azobisisobutyronitrile (AIBN) and CdSe QDs were used at 0.50 and 0.75% and 0.075, 0.15 and 0.225%, both with respect to monomer content, respectively. Table 1 shows the different treatments implemented. First, a surfactant solution of CTAB and water (20 g) was prepared into the reactor. To obtain the miniemulsion a hydrophobe mixture containing the CdSe QDs, styrene monomer, hexadecylamine, hexadecane and the initiator was charged into the reactor. The mixture was sonicated for 2 min at 40% amplitude (Sonic dismembrator FB-505). The polymerization process was achieved at 70°C with continuous magnetic stirring in nitrogen atmosphere.

## Characterization

The average particle size, particle size distribution and polydispersity index of polymer particle was determinate by statistic method considering the measurement of at least 500 particles. Latexes micrographs were obtained by a transmission electron microscope Jeol JSM-7401F. Photoluminescence (PL) spectra of CdSe/polystyrene latexes were acquired using a Varian Eclipse spectrofluorometer at 360 nm excitation.

	Surfactant	Initiator	CdSe		Surfactant	Initiator	CdSe
Treatment	CTAB	AIBN	QDs	Treatment	CTAB	AIBN	QDs
	(M)	(%)	(wt%)		(M)	(%)	(wt%)
1	0.0016	0.50	0.075	10	0.0016	0.75	0.075
2	0.0016	0.50	0.150	11	0.0016	0.75	0.150
3	0.0016	0.50	0.225	12	0.0016	0.75	0.225
4	0.0032	0.50	0.075	13	0.0032	0.75	0.075
5	0.0032	0.50	0.150	14	0.0032	0.75	0.150
6	0.0032	0.50	0.225	15	0.0032	0.75	0.225
7	0.0054	0.50	0.075	16	0.0054	0.75	0.075
8	0.0054	0.50	0.150	17	0.0054	0.75	0.150
9	0.0054	0.50	0.225	18	0.0054	0.75	0.225

Table 1. Conditions of the synthesis process by miniemulsion polymerization for the different treatments.

# **Results and Discussions**

The latexes obtained were stable and showed fluorescence by excitation with UV light, indicating that the method used prevented QDs deactivation also known as quenching. It was observed that as effect of the different treatments, the latexes displayed fluorescent emission with different intensity. The variations in the surfactant concentration influenced the polymer particle size in the latex; these variations affected the positioning of the QDs in the matrix and consequently the compound fluorescent emission.

#### MACROMEX 2011

In order to quantify the effect of the different treatments on the fluorescence emission, photoluminescence spectra of the latexes were obtained. It was observed a stable emission at 580nm at 360nm excitation wavelength for all treatments. The fluorescence intensity was in correlation with the synthesis parameters. Figure 1 shows the photoluminescence emission spectra of the latexes with the different treatments. Emission intensity presented changes with respect to synthesis parameters. The higher QDs concentration presented higher emission intensity, this behavior was already reported by Joumaa et al. [3], specifying that emission intensity increased with the concentration of QDs.

Average particle diameter (Dn), particle size distribution (PSD) and polydispersity index (I) were calculated from a statistical study performed on at least 500 polymer particles. Table 2 shows the results of the different response variables obtained from the different treatments. The values of I were found to be narrow for all the treatments, presuming the stability of the miniemulsion systems during the polymerization. This can be corroborated by the STEM images obtained from the latexes (Figure 2).

The increment in surfactant concentration produced the decrement in Dn. However, the effect of varying the initiator concentration did not affect significantly Dn. The fluorescent emission of the latexes varied as a consequence of variations on both surfactant and initiator concentration. These values also affected directly the final number of polymer particles (Np) per unit volume. Considering that, the number of QDs per polymer particle also was affected. The relationship of QDs-polymer particle was theoretically calculate taking into account the number of CdSe per cubic centimeter determinated by polymer average particle size and the amount of dots incorporated in the synthesis process.



Figure 1. Photoluminescence emission spectra of CdSe-polystyrene latexes.



Figure 2. Micrograph scanning electron microscopy in transmission mode of CdSe-PS latex

	Table 2.	Characteristics	of CdSe-p	olystyrene	latexes obtained l	by miniemulsion	polymerization.
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Treatment	Dn (nm)	Ι	Np (cm3)x10-16	QDs/ polymer particle
1	139	1.01	0.821	0.2161
2	134	1.02	0.896	0.3949
3	138	1.01	0.840	0.6350
4	124	1.01	1.42	0.1249
5	131	1.01	1.22	0.2900
6	129	1.01	1.27	0.4200
7	101	1.02	3.89	0.0456
8	97	1.04	4.10	0.0863
9	102	1.04	3.76	0.1418
10	141	1.01	0.982	0.1806
11	144	1.01	0.917	0.3859
12	144	1.02	0.907	0.5881
13	110	1.02	3.06	0.0579
14	109	1.03	3.07	0.1152
15	109	1.03	3.06	0.1743
16	110	1.03	3.00	0.0591
17	106	1.02	3.65	0.0960
18	96	1.03	4.87	0.1095

The results obtained indicate that the QDs were not uniformly distributed among the latex particles, since the number of dots per polymer particle was not directly proportional to the fluorescence emission intensity. These facts let us to consider that there was no homogeneous encapsulation of dots by polymer particles and that there were dots which were not encapsulated and they could be degraded during the process.

#### Conclusions

The emission results obtained revealed a successful encapsulation of nanoparticles in the polymer matrix. The emission intensity of the CdSe-polystyrene latexes underwent changes due mostly to the changes in the polymer particle size, induced by variations in the levels of surfactant and initiator used, and the number of QDs encapsulated per polymer particle.

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# AMINO ALCOHOL FUNCTIONALIZED POLYETHYLENE AS COMPATIBILIZER FOR POLYETHYLENE NANOCOMPOSITES

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#### Abstract

The compatibilization effects provided by Itaconic Acid (IA), Maleic anhydride (MA) and 2-[2-(dimethylamine)ethoxy]ethanol (DMAE) functionalized polyethylenes for forming polyethylene-based nanocomposites were studied and compared. IA and MA were grafted into PE by melt mixing to obtain polyethylene grafted itaconic acid (PEgIA) and polyethylene grafted maleic anhydride (PEgMA). Amino alcohol functionalized polyethylene was prepared by reaction of PEgIA or PEgMA with DMAE in the melt to form polyethylene grafted dimethyl amine ethoxy ethanol (PEgDMAE). Nanocomposites were prepared by melt processing using a twin screw extruder by blending polyethylene and these compatibilizers, with two quaternary ammonium surfactant modified montmorillonite clays (Cloisite 30B and 20A). FTIR characterization confirmed the formation of these compatibilizers and confirmed the reaction between PPgIA or PEgMA and the amino alcohol. All the compatibilized nanocomposites had better clay exfoliation compared to the uncompatibilized PE nanocomposites. Mechanical properties, X-Ray diffraction and transmission electron microscopy results showed that the PEgDMAE with C20A formed better exfoliated-intercalated nanocomposites. Samples with C30B did not showed any dispersion or intercalation improvement which was attributed to the thermal degradation of the surfactant and the lower initial intergallery spacing of this clay.

#### Introduction

Polyethylene is one of the most widely used polyolefin polymers because of its low cost, low weight, low-temperature toughness, low moisture absorption, good optical properties and ease of processing and recycling. However because it does not include any polar group in its backbone, it is difficult to get the exfoliated and homogenous dispersion of the clay layer at the nanometer level in the polymer matrix. Polyolefin-clay nanocomposites shows improved properties such as mechanical, dimensional, barrier to different gases, thermal stability and flame retardant enhancements with respect to the bulk polymer [1-3]. Clay exfoliation has been achieved by compounding organo-modified montmorillonite (MMT), using maleic anhydride grafted polyethylene (PEgMA) and PE by melt compounding [4,5]. However, the potential use of itaconic acid, a vinyl monomer containing two carboxylic group and its derivatives have been investigated for this purpose [6]. The application of itaconic acid can be considered interesting because of their carboxylic bifunctionality and because itaconic acid is produced from non-oil based renewable natural resource, i.e. by large scale fermentation of molasses, a by-product from sugar industry. Other studies have demonstrated the limited capacity of maleated polyolefins as in situ compatibilizers to exfoliate organoclay by a melt compounding approach [7-9]. Itaconic anhydride is a chemical compound that presents a closed ring which can be easily opened by temperature or mechanical stress to form itaconic acid also known as methylen-succinic acid which is one of the three acids obtained from the distillation of the citrus acid. Opposed to the maleic anhydride, IA is one of the few acids produced in the nature by microorganisms which give him non-toxic characteristics. The purpose of the present work is to explore the possibility of other functional PE's that might serve as better compatibilizers than maleated PE. The reaction of PEgIA with an amine alcohol may be used to generate a PEgDMAE that, in theory, may interact with the anionic surface of the organo clay lowering its surface energy and enhancing its dispersion on the polymer

matrix [10]. The ability of these modified PE compatibilizers to exfoliate and disperse two different organo clays was examined in this work.

### Experimental

PE matrix polymer is of commercial grade from Dow Plastics (LDPE 133A) with a melt index of 0.22g/10min. The PEgIA used was obtained in our lab by melt grafting using Itaconic Acid from Sigma-Aldrich and Di-cumyl peroxide from Sigma-Aldrich as initiator. The PEgIA obtained contains 0.4 wt% IA. The MMT organoclay used was one modified with a dimethyl, dihydrogenated tallow quaternary ammonium salt (Closite 20A, non-polar) and other with Nmethyl, tallow bis-2-hydroxietyl, ammonia chloride (Cloisite 30B, more polar) from Southern Clay Products Co. A tertiary amino alcohol, DMAE, 2-[2-(dimethylamino)-ethoxy] ethanol and 2,6-Di-tert-butyl-4-methylphenol (BHT, 99%) from Sigma-Aldrich, which were reagent grade and were used without further purification. The grafting of IA into PE was carried out using a method previously reported [10]. In order to prepare the amino alcohol modified PE used as compatibilizer, the obtained PEgIA was previously dried at 90°C for 24 hours and was premixed in presence of BHT within a Banbury batch mixing chamber (Brabender PL2000) equipped with roller rotors. After 2 min of mixing and when all the polymer was melted, the amino alcohol (DMAE) was added, in sealed PE bags in order to avoid their evaporation, and the mixing was continued for 12 min at 170°C and 60 rpm, forming the PEgDMAE. Nanocomposites were prepared by compounding the required amounts of PEgIA or grounded PEgDMAE, LDPE and organoclay (C20A or 30B) with 500 ppm of BHT in a Werner and Pfleiderer twin screw extruder, with an L/D=29:1 and D=30 mm, operating at 190°C and 100 rpm in co rotating mode. Samples were prepared by compression moulding at 190°C. The Fourier transform infrared spectra were recorded on a Nicolet 550 at 4cm-1 of resolution and 30 scans. X-ray diffraction of the clays and nanocomposites, in order to evaluate the evolution of the clay d001 reflection, was performed in a Siemens D5000 using CuKa X-ray radiation. The X-ray samples were obtained from compression moulding in order to avoid the preferred orientation of the clay. Ultrathin section for STEM analysis, approximately 70-100 nm in thickness, were cut from compression moulded samples, with a diamond knife at a temperature of -95°C using a Leica microtome attached to a closed chamber with circulating liquid N2. The STEM observations were performed with a Jeol-JSM7104F with a STEM modulus and a field emission gun at an accelerating voltage of 200 kV. Tensile properties were analyzed on an Instron model 4301 upgraded for computerized data acquisition. Moduli were determined using an extensometer at a crosshead speed of 0.51 cm/min.

#### **Results and Discussion**

The characterization by FTIR of the amine modified PE's (figure 1-a) showed the disappearance of the carbonyl stretching absorption at 1720 cm-1 associated with the carboxylic acid of IA, indicates a considerable extent of reaction between IA and the amino alcohol. For the PEgDMAE (Figure 1-b) new absorption bands at 1740cm-1 and 1780 cm-1 can be observed which are associated with the ester functionality.

The X-ray diffraction patterns of the neat clay (C30B) and nanocomposites with compatibilizing agents are shown in figure 2. The original basal reflection peak of 30B in samples with 5% of clay and both compatibilizers is shifted to higher angles, from  $4.9^{\circ}$  to  $5.8^{\circ}$  (1.80 to 1.51 nm). This indicates that this clay induce a poor intercalation to these composites. Some authors [11]

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suggests that even though this clay has a surfactant with more polar groups, the degree of saturation of the exchangeable cations and the lower initial intergallery spacing (1.8 nm) are the main factors affecting this nanoclay exfoliation. On the other hand, all the samples with C20A (Figure 3) show a shift of the diffraction peak to lower angles and higher intergallery spacing from 2.4 nm for the original C20A clay to 3.0 nm for PEgIA whereas the reflection peak of the sample with PEgDMAE compatibilizer disappear. This indicates that the ordered structure of the layered mineral clay was effectively eliminated. This fact reveals that the clay was more efficiently intercalated and dispersed in the PE matrix, when using these compatibilizers, especially when using PEgDMAE. The inspection of STEM images confirmed the observed behavior obtained by XRD.



Figure 1. FTIR spectra for: a) PEgIA and b) PEgDMAE

Clay exfoliation is clearly evident in the image shown in Figure 4-a, for sample with 5 wt% of C20A and 20 wt% of PEgDMAE as compatibilizer, where a more uniform distribution with less tactoids can be seen. These are indicative of a greater degree of exfoliation of this clay, as suggested by the XRD results. No peak was generated by these composites. The image for C20A clay and PEgIA as compatibilizer composite (Figure 4-b), on the other hand, show more clay aggregates or tactoids than the sample with PEgDMAE. These results are also consistent with those from XRD, where this compatibilizer showed a shift to lower 2 $\theta$  angles.

Table 1 shows mechanical properties for the nanocomposites. Modulus is only slightly increased when using PE-clay without compatibilizing agent. Mean while all the samples with compatibilizers have higher modulus. The greatest improvement was for the PEgDMAE samples, with an increase of around 70% compared to pure PE. This means that the addition of PEgDMAE could intercalate or exfoliate the C20A more easily and thus significatively increase the stiffness of the PE. This confirms the fact that PEgDMAE, because of its functional ionic polar groups, could be interacting directly with anionic surface of the clay or with the functional groups in the surfactant allowing more intercalation. This compatibilizer showed a better performance than polyethylene grafted maleic anhydride (PEgMA) compatibilizer since nanocomposites using PEgMA using these same clays, reported in figure 3-e, show a diffraction peak indicating less clay exfoliation than PEgDMAE in which no peak was observed.



**Figure 2.** XRD patterns for: a) C30B and PE/Clay nanocomposites at 5%, b) sample (a) and 20% of PEgIA and (c) sample (a) with 20 % of PEgDMAE.



**Figure 3.** XRD patterns for: a) C20A and PE/Clay at 5% of clay, b) sample (a) with 20wt% of PEgIA, c) sample (a) with 10% PEgDMAE, and d) sample (a) with 20wt% of PEgDMAE and (e) sample with 20wt% of PEgMA



**Figure 4.** STEM images of nanocomposite samples using 5% of clay and 20 wt% of: (a) PEgDMAE and (b) PEgIA as compatibilizer.

	Modulus	Stress at Break
Sample	(MPa)	(MPa)
PE	$208.2 \pm 4$	12.4 ±0.8
PE/Clay5	214.4 ±1	13.5 ±1.0
PE/PEgIA-10/Clay5	293.9 ±3	16.5 ±1.5
PE/PEgIA-20/Clay5	$345.0 \pm 1$	$17.2 \pm 0.9$
PE/PEgDMAE-10/Clay5	342.9 ±4	16.2 ±0.9
PE/PEgDMAE-20/Clay5	$370.0 \pm 2$	17.5 ±0.8

Table 1. Mechanical properties of the nanocomposites.

#### Conclusions

In this work PE/clay nanocomposites using PEgIA and PEgDMAE as compatibilizers have been obtained. FTIR confirmed the formation of these compatibilizers and confirmed the reaction between PPgIA and the amino alcohol. Clay dispersion and interfacial adhesion were strongly affected by the kind and interactions of compatibilizer. Mechanical properties, X-Ray diffraction and transmission electron microscopy results showed that the PEgDMAE with C20A formed better exfoliated-intercalated nanocomposites than samples with C30B. The ionic functionality of PEgDMAE improved the clay intercalation-exfoliation capacity of the polymer and enhanced the mechanical properties.

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