Functionalized Multi Wall Carbon Nanotubes with Polymer Prepared *vía* "Nanotubes Salts"

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INTRODUCTION

There are in the automotive and aerospace area opportunities to application of new polymeric materials based on CNT. The CNT potentially provides to materials, properties of strengthen and conductivity higher than those obtained with fiber glass, carbon black and graphite. [1,2] The covalent functionalization of carbon nanotubes is an alternative to disperse them in organic solvents and polymer matrixes[3,45] but when the CNT have high functionalization degree, the π-conjugates network of graphite is destroyed which is at the expense of mechanical and electrical properties of composites resulting. [6,7] Research groups have worked about effects of reinforcement of polymers using CNT. T. Mo *et al*., [8] have studied the compatibility of MWNT with poly-imide, the dispersion improved into matrix when the MWNT were functionalized with acid groups. R.B. Mathur *et al.,* [9] have studied the strengthen of thermoplastic incorporing MWNT and MWNT pretreated with acid groups, the 10% v of MWNT increases the flexural modulus at 25% respect to polymer and increases 17% with MWNT pretreated with acid groups. A. Kwabena *et al.*, [10] mention that the MWNT produce nucleating effect in polyethylene oxide increasing crystallinity. They mention that the mechanical properties of polymer with load of no-agglomerated MWNT were marginally higher than the polymer with a load of MWNT agglomerated.

We present the characterization of nanocomposites prepared via "nanotubes salts" containing functionalized carbon nanotubes with polymer (polymer-CNT). The procedure is a one-step method and polymer chains covalently linked to MWNT are obtained. The characterization of polystyrene-MWNT nanocomposites was conducted with Raman spectroscopy, SEM and TEM, also was used thermal characterization with DSC and TGA. A twin-screw mixer was used to prepare composites by mixing of functionalized CNT with polymer (prepared with "nanotubes salts" reaction) and a polymeric matrix. The composites were observed through SEM to study the interaction between CNT and polymer.

OBJETIVE

Our objective was to develop the mechanical characterization of polymeric nanocomposites obtained by "nanotubes salt" reaction and to prepare composite of polymers with CNT using the *melt mixing methods* and to develop the thermal and mechanical characterization of resulting composites.

EXPERIMENTAL

Materials and Methods

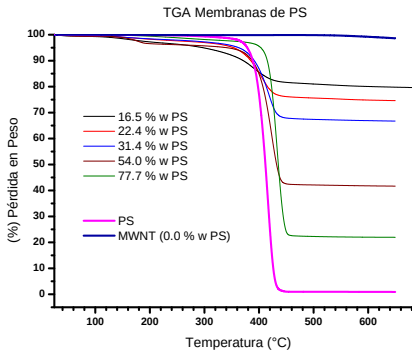


Figure 1. TGA of nanocomposites obtained *via* "nanotubes salts" reaction.

MWNT was produced in our laboratory through chemical vapor deposition (CVD). For MWNT synthesis, following conditions were used: 2.5 % w ferrocene and 1% w ethylic alcohol in toluene, argon flow rate 2.5 L/min, temperature 820 °C for 1 hour.[11] MWNT were purified as mentioned in Alvizo-Paez *et al.*[12] Styrene was obtained from Fluka and was used as received. Was used Li granulated with high Na purchased from Aldrich. THF obtained from Aldrich was dried before use by refluxing with $LiAlH_4$. All others solvents were acquired from Aldrich.

Raman spectra were collected from solid sample using a microRaman inVia Renishaw system, with 633 nm laser source. HR-TEM images were taken with a JEOL JEM-2010 FEF at 200 KV. SEM images were obtained using a Philips FEG-XL30 MEB, field emission scattering electron microscope. Dynamic mechanical analysis DMA861^e METTLER TOLEDO was used in order to know mechanical behavior of functionalized MWNT and the glass transition temperature through storage module and Tan δ curves respectively. The sample was tested in tension mode at 1 Hz of frequency with controlled force and heating from 25 to 150 ºC to 2 ºC /min. TGA Q5000 of TA instrument was used to study the polymer weigh fraction coating the carbon nanotubes.

General Procedure of polymerization

In a 1000 ml three neck round-bottomed flask, previously dry with flame and under an inert atmosphere (argon), was condensed ammonia (NH_3) 500 ml approximately. 300 mg of Li was added to the NH_3 into reactor and stirred with magnetic bar, using a cryogenic bath. 30 mg purified MWNT previously dispersed through sonication in tetrahydrofuran (THF) and 2gr styrene dissolved in THF were simultaneously added to the reaction mixture. The reaction mixture was stirred with a homogenizer for 10 minutes. Cryogenic bath was removed to evaporate the ammonia. The reaction product were purified using 2L HCl 5% and 50 ml of chloroform and finitely the purified product was filtered, dried and weighed.

Preparation and Characterization of Composites by melt mixing methods

The functionalized carbon nanotubes with PS were mixed with polystyrene using a mixer MiniLab HAAKE Reomex CTW5. Were mixed 50 mg of PS-MWNT and 4.95 gr of PS using 10 min of residence at 150°C to obtain composites The material obtained was molded at 150 °C, the films were with thickness from 0.30 mm to45mm. The thermal properties of composite were determined using DSC, TGA, DMA; the behavior of fracture was studied with INSTRON and SEM.

RESULTS

Characterization of nanocomposites of functionalized carbon nanotubes with polystyrene PS-MWNT

Was determined the amount of polymer on functionalized nanotubes with TGA. In Figure 1 we can be seen the lost weight of polymer also the reference curves of pure PS and unfunctionalized MWNT.

We can see in figure 1 five different samples with different amount of PS, the graphic shows the functionalization degree in the MWNT from 16.5w% to 77.7 w % of PS. The Figure 2 presents the first

derivative of the TGA where maxim temperature corresponds to the temperature which the degradation rate of the polymer is higher. It is noted in the graphic that when MWNT weight fraction is lower in nanocomposites the degradation temperature increase indicating no-agglomeration and better dispersion of nanotubes so thermal stability enhance for nanocomposito up 33 °C. The weight fraction to 179 °C and 260 °C were attributed to polymer chains intimately linked to the wall nanotubes by van der Waals attraction and they can move and evaporate before the degradation temperature of polymer. These movements are most evident in the DSC curves. In Figure 3 we can see the DSC curves of pure polymer and nanocomposites with varying degrees of functionalization. Figure 3 present Tg of pure PS at 100 °C, in the case of nanocompositos there are two transitions, one for PS formed by the reaction at 105 °C suggesting that the Tg increases 5 °C. Another transition near 96 °C suggests that linked polymer chains to wall nanotubes by van der Waals interactions presented movements before the Tg,

With Raman spectroscopy we can observe the shift of "*D*" band of MWNT in different nanocompositos containing different weight fraction of PS The intensity of band "*D*" increased up to three times indicating that disorder interrupted the π-conjugation C=C on wall of MWNT. Also the band "*D*" presented displacement in all cases (see insert graphic) from 5 cm^{-1} to 22 cm^{-1} suggesting that the atoms of carbon with sp^2 hybridization has been changed to carbon sp^3.
See table 1.

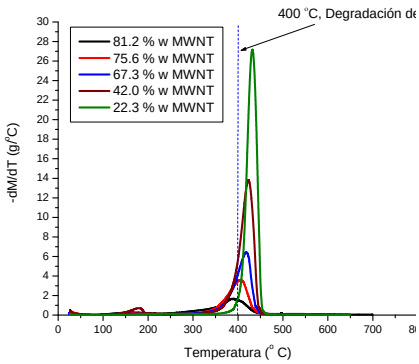


Figure 2. First derivative of the TGA of nanocomposites of PS obtained *via* "nanotubes salts" reaction.

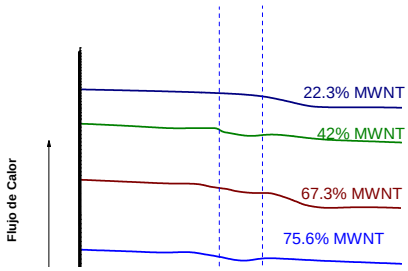
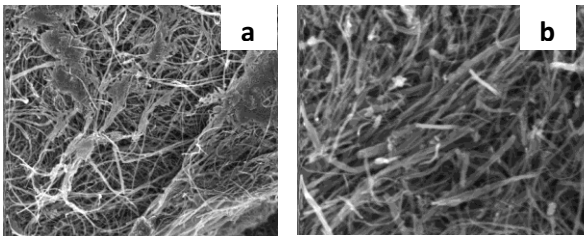


Figure 3. DSC of pure PS and nanocomposites of polystyrene obtained *via* "nanotubes salts" reaction

Nanocomposito	I_D/I_G	ΔD (cm^{-1})	ΔG (cm^{-1})
MWNT (0%w polímero)	0.49	-	-
PS-MWNT (16.5%w PS)	1.49	- 22.0	+ 0.9
PS-MWNT (22.4%w PS)	1.75	-5.2	- 1.8
PS-MWNT (31.4%w PS)	1.43	-9.0	+ 5.3
PS-MWNT (54.0%w PS)	1.47	-7.0	+ 1.0
PS-MWNT (77.7%w PS)	1.35	-21.0	+3.6

Table 1. Nanocomposites with diferentes levels of functionalization. Show I_D/I_G, shift "*D*" band and ΔD in cm^{-1} of "*D*" band.

Whit SEM microscopy we can clearly to observe the effect of coating of polymer on nanotubes. When the weight fraction of the PS increased, the MWNT were mostly coated for polymer and dispersed. Figure 4.



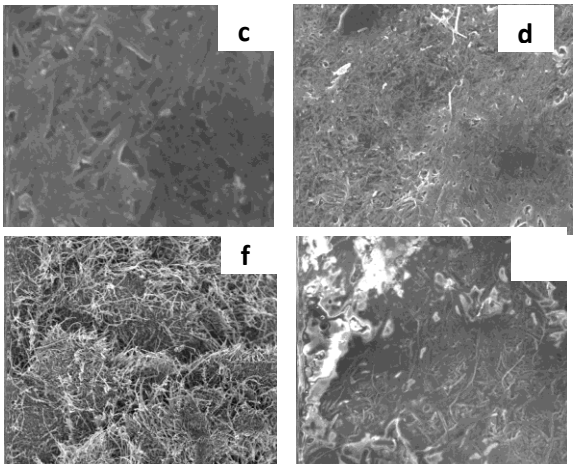
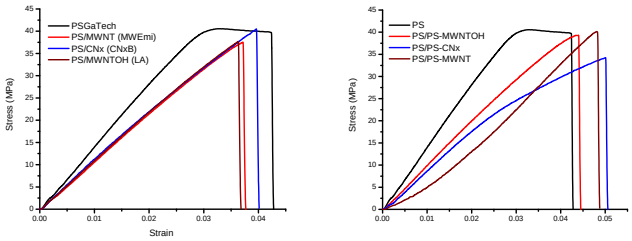


Figure 4. SEM of PS. a and b nanocomposite with 81.2%w de MWNT, c and d 75.5%w de MWNT, e and f 67.3%w de MWNT, g and h 42.0%w de MWNT e i and j 22.3%w de MWNT.

Figure 5. Tension probe of composites made by *melt mixing* and *methods* with MWNT functionalized. PS-MWNT Plasticizing effect is evident in both type of composites.



The melt mixing give composites and were probed by INSTRON in order to determine the fracture behavior. Figure 5 show the tension probe for all composites prepared. All type of composites presented plasticizing effect.

CONCLUTIONS

Was possible to prepare nanocomposites with MWNT and PS-MWNT *via* "nanotubes salts" with polymers chains linked covalently on wall of MWNT. We prepared composites with MWNT and PS-MWNT which presented plasticizing.

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