

EFFECT OF CROSSLINKING AGENT IN CORE-SHELL POLYMERS OF POLYSTYRENE AND POLY(BUTYL ACRYLATE).

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1. Abstract

Polystyrene (PST) and poly(butyl acrylate) (PBA) core-shell polymers were synthesized by two-stage microemulsion polymerization. When styrene is polymerized in the first stage to produce the core and butyl acrylate is added in the second stage, some phase inversion occurs because the minimum interfacial free energy for this situation corresponds to the inverted core/shell morphology. We studied the effect of crosslinking agent divinyl benzene in the core-shell polymers of polystyrene and poly(butyl acrylate) to treat to avoid phase inversion. The core-shell polymers prepared were characterized by quasielastic light scattering (QLS), transmission electron microscopy (TEM), and mechanical analysis (tensile and hardness). The results show that microemulsion polymerization produce latex with small particle size (< 30 nm) and high conversion (> 85 %), TEM and tensile-stress shows that in the polymers synthesized with crosslinking agent divinyl benzene the phase inversion don't occur.

2. Introduction

Core/shell polymers are attracting scientific and industrial interest because their chemical and mechanical properties can be tailored for applications such as paints, adhesive, paper and textile manufacturing, and impact modifiers [1-4]. Core/shell polymers are usually made by emulsion and microemulsion polymerization in two-stage process; first one monomer is polymerized to form the core, then the second monomer is added in batch or semi-continuously and polymerized over the seed particles to form the shell. One of the polymers has a much lower glass transition temperature (T_g) and the other a higher T_g than the temperature at which the material is being used [5-7].

Pérez-Carrillo et. al. reported that when styrene was polymerized in the first stage to produce the seeds and PBA was added in the second stage, some phase inversion occurs because the minimum interfacial free energy for this situation corresponds to the inverted core/shell

morphology [8, 9]. In this work we investigate the effects of crosslinking agent divinyl benzene in core-shell polymers of polystyrene and poly(butyl acrylate) to treat to avoid phase inversion.

3. Experimental section

Cetyltrimethylammonium bromide (CTAB), 99% pure from Aldrich. Styrene and butyl acrylate, 99% pure from Scientific Polymer Products (SPP) were passed through a TR-7 or a HR-4 column (SPP) to remove their inhibitors. Allyl metacrylate (ALMA), 98% pure, and divinyl benzene (DVB), 80% pure, both from Aldrich, were used as crosslinking agent and compatibilizer. 2,2'-Azobis(2-amidinopropane) hydrochloride (V-50) from Wako Pure Chemical Industries, 99.5% pure. Hydroquinone, 99% pure from Productos Químicos Monterrey. Doubly distilled and de-ionized water was employed.

Core shell polymers were made in automatic reactor (Automated Chemical Reactors and Calorimeters) from HEL. First the latex of PST were produced by the polymerization at 60 °C and 200rpm in microemulsion containing 1 wt.% CTAB, 10 wt.% monomer ($w_{ALMA}/w_{monomer} = 0.01$) ($w_{DVB}/w_{monomer} = 0.05$) and 88.86 wt.% water, initiated with V-50 ($w_{V-50}/w_{monomer} = 0.01$), followed by the semi-continuous addition of more monomer. Before adding the other monomer to form the shell, the latex were diluted with water to 10% wt.% solids. In the second stage, the needed amount of BA was added semi-continuously to form the shell over the PST seeds. The reacting system was sparked with argon throughout the reaction.

Particle size was measured with Malvern 4700C QLS apparatus at room temperature. The latex particles were examined in a JEOL 1010 transmission electron microscope (TEM). Tensile tests were performed at room temperature according to the ASTM D-638 method in a universal testing machine (United). Hardness test were performed according to the ASTM D224 method in a hardness Shore A de PTC Instrument, model 306L.

4. Results and discussion

Table 1 shows the conversions and the z -average particle size (Dp_z) measured at the end of stage 1 and 2 for the core-shell polymers of PST/PBA with or without DVB. In all the cases we observed conversions larger to 90% this indicates that the probability to form copolymers in the second stage is low. In the case of average particle size we observe that the size are larger at

the end of the second stage, this growth suggest that the monomer added during the second stage polymerizes over the seed particles to form a core/shell structure. However, this growth does not exclude the formation of other morphologies or additional homo-polymer particles.

Table 1 Conversion and average size at the end of stage 1 and 2

Core/Shell	Composition	Conversion (%)		Dp_z		
		Stage 1	Stage 2	Stage 1	Stage 2	Stage 2 estimated
PSt-PBuA	40/60	93	93	23	29	32
PSt-PBuA	60/40	93	91	23	29	26
PSt-PBuA*	40/60	95	92	16	21	22
PSt-PBuA*	60/40	91	87	24	27	29

* Whit DVB

Figure 1 present the stress-strain curves from core/shell polymers of PST/PBA weight ratio 40/60 synthesized with or without DVB. Fig. 2 depicts stress-strain curves from core/shell polymers of PST/PBA weight ratio 60/40 synthesized with or without DVB. Both pictures show that the polymers whit DVB exhibits smaller yield stress and higher elongation. The large strength and the low elongation of the material without DVB to indicate that the phase inversion is occur and the PST go to the core to the shell, this cause we have a more rigid material.

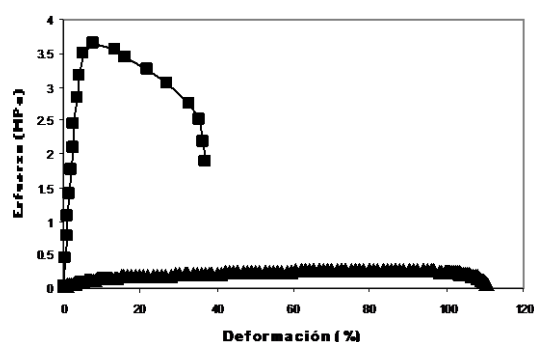


Fig. 1 Stress-strain curves of core/shell polymers with PST/PBA weight ratio of 40/60 with (▲) or without DVB (■).

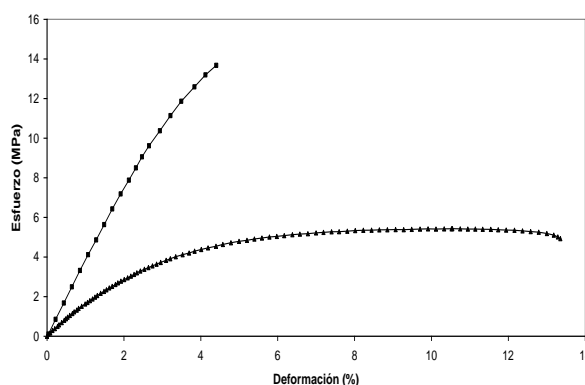


Fig. 2 Stress-strain curves of core/shell polymers with PST/PBA weight ratio of 60/40 with (▲) or without DVB (■)

TEM confirm the core/shell morphology. Fig 3 depicts pictures of the latexes of PST/PBA (40/60 w/w) synthesized without DVB (a) or with DVB (b), where the light and dark domains correspond to the PBA y PST regions, respectively. The picture 1a show the form that is structured the particles obtain without DVB, here we can observe perfectly the core of PBA and the shell of PST, but this in not so evident in the picture 1b, here we only can observe the PBA structure, this can be because the PBA shell is so gross that not permit the access of the electrons to the core of PST, and this not permit to see the polymer under condition of preparation.

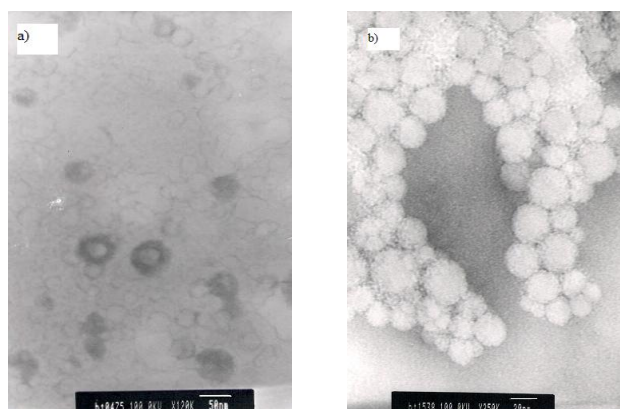


Figure 1 TEM photographs of PST/PBA core/shell particules (40/60 w/w).

5. Conclusions

The presence of divinyl benzene in the seeds of PST to avoid phase inversion.

6. References

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