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NANOSTRUCTURED UNSATURATED POLYESTER USING BLOCK COPOLYMERS: MORPHOLOGY, OPTICAL PROPERTIES AND FRACTURE TOUGHNESS RELATIONSHIP

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ABSTRACT

Novel nanostructured unsaturated polyester thermosets modified with two poly(ethylene oxide-*b*-propylene oxide-*b*-ethylene oxide) block copolymers, were developed. Effects of molecular weights and blocks ratio on optical and mechanical properties were reported. It was found that self-assembly or polymerization-induced phase separation mechanisms were followed by the nanostructured thermosetting systems to achieve the final morphology. Relationships between final morphology and optical and mechanical properties of thermosets were examined.

Keywords: *Unsaturated polyester, Block copolymers, Self-assembly, Fracture toughness*

RESUMEN

Se desarrollaron termoestables nanoestructurados de poliéster insaturado modificados con dos copolímeros de bloque tipo poli(óxido de etileno-*b*-óxido de propileno-*b*-óxido de etileno). Se reportaron efectos del peso molecular y relación molar de los bloques sobre propiedades ópticas y mecánicas. Se demostró que la morfología de los termoestables siguió como mecanismos para nanoestructurarse, autoensamblado o separación de fases inducida por polimerización. Se estudió la relación de la morfología de los termoestables con sus propiedades ópticas y mecánicas.

Palabras Clave: *Poliéster insaturado, Copolímeros de bloque, Autoensamblado, Tenacidad a la fractura*

1. INTRODUCTION

Unsaturated polyester (UP) resins comprise more than 80 % of the global market of resins for composites [1]. Block copolymers (BCP) have been used to control the morphology of thermosets due their capacity to segregate at the nanometer scale [2]. In a UP/BCP system, the resin could acts as a solvent or as a selective solvent for the BCP. In the first case, the domains are formed by polymerization-induced phase separation (PIPS) and in the latter case by self-assembled micelles before curing [2,3]. The present work attempted to study relationships between morphology, optical and mechanical properties of an UP resin as a function of the PEO-*b*-PPO-*b*-PEO block copolymer and content.

2. EXPERIMENTAL

2.1. Materials and Blending Protocol

A commercial orthophthalic UP resin with the trade name Cristalan® manufactured by Andercol S.A. was used. Poly(ethylene oxide-*b*-propylene oxide-*b*-ethylene oxide) block copolymers (BCPs) with trade names Pluronic® were used. These block copolymers have a structure $E_xP_yE_x$, where the subscripts indicate the number of repeated units of E = ethylene oxide and P = propylene oxide. The structures were $E_{75}P_{34}E_{75}$ and $E_{20}P_{69}E_{20}$ denoted here as EPE75 and EPE20, respectively. Mixtures were denoted as follows: the 5%EPE75 mixture contained 5 wt % of EPE75 and 95 wt % of UP. The reacting mixtures were prepared adding 1.5 phr of MEKP. The mixtures were cured following isothermal curing cycles precured at 80 °C during 3 h and postcuring at 170 °C during 3 h.

2.2. Experimental Techniques

2.2.1 Differential Scanning Calorimetry (DSC). DSC measurements were performed in a Perkin Elmer DSC-7 calorimeter. The samples were first heated from 25 °C to maximum of 80 °C, followed by a cooling to -95 °C at 1 °C min^{-1}, and finally heated at 10 °C min^{-1}.
2.2.2 Optical microscopy. Transmitted light intensity were performed using a Nikon Eclipse E600W coupled with a hot stage Mettler FP 82 HT.
2.2.3 Dynamic light scattering (DLS). DLS measurements were done in a Brookhaven BI-200SM goniometer with a 9000AT correlator.
2.2.4 Dynamic mechanical analysis (DMA). DMA measurements were done using a GABO Eplexor 100 N with a three-point bending device having a span length of 20 mm.
2.2.5 Atomic Force Microscopy (AFM). Morphology of cured mixtures was analyzed using AFM with a scanning probe microscope (SPM) (NanoScope IIIa Multimode from Digital Instruments, Veeco Instruments, Inc) in tapping mode (TM-AFM).
2.2.6 UV-vis measurements. UV-vis transmittance spectra of thermosetting mixtures were obtained using a spectrophotometer Shimadzu UV-3600 in the spectra range from 300 to 800 nm.
2.2.7 Mechanical Properties. Three-point bending and fracture toughness tests were performed following ASTM D 790-0 and ASTM D 5045-99 standards, respectively.

3. RESULTS AND DISCUSSION

3.1. ***Nonreactive mixtures.*** Figure 1 shows the visual appearance of neat UP and nonreactive 15%EPE75 and 15%EPE20 mixtures. As can be seen, no visual changes were observed after the modification of UP with the BCPs before curing indicating a lack of macrophase separation.

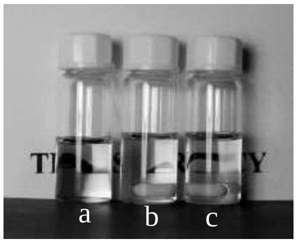

Figure 1. Visual appearance of (a) neat UP and nonreactive (b) 15%EPE75 and (c) 15%EPE20 mixtures.

Figure 2 shows the DSC measurements of nonreactive UP/EPE75 and UP/E182 mixtures. The nonreactive UP/EPE75 mixtures exhibited a single T_g with values between T_gs of the components indicating high miscibility. In the nonreactive UP/EPE20 mixtures two T_gs were detected outside of the T_gs of the components denoting phase separation and possibly self-assembled micelles.

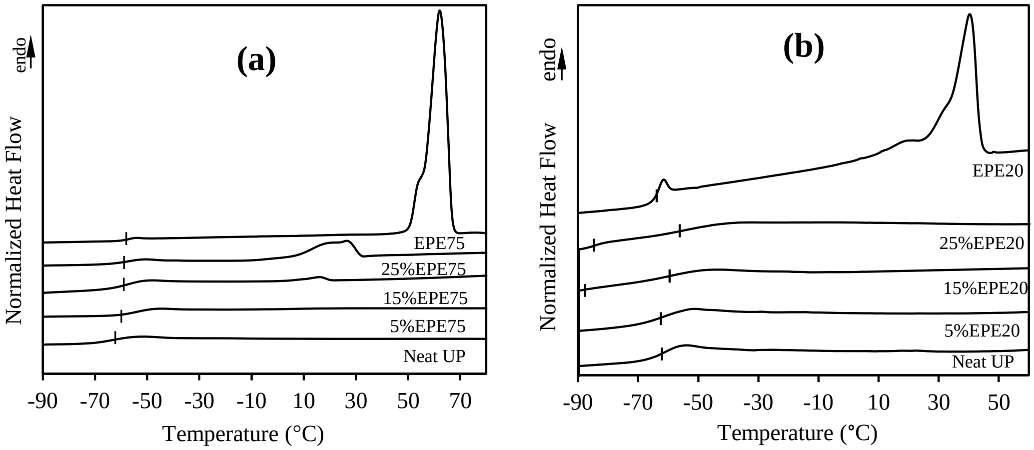

Figure 2. DSC thermograms for nonreactive (a) UP/EPE75 and (b) UP/EPE20 system.

In order to investigate the dynamics of mixtures, DLS measurements were carried out. The neat UP resin and the nonreactive 5%EPE75 mixture showed similar dynamics (i.e. with no autocorrelation functions ($g_2(t)$) were obtained). Figure 3 shows the normalized $g_2(t)$ obtained for the 5%EPE20 mixture, which verify the formation of self-assembled micelles at nanoscales [4].

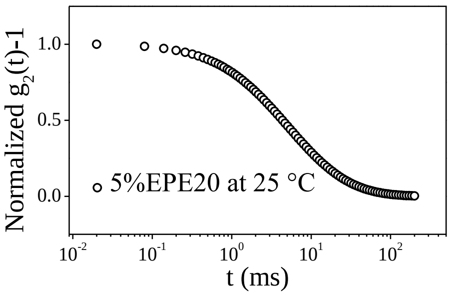

Figure 3. Intensity correlation function versus time for nonreactive 5%EPE20 mixture.

3.2. ***Cured Mixtures***. Figure 4 shows the changes in the transmitted light intensity during curing for neat UP and 25%EPE20 mixture. On the contrary, the UP/EPE75 mixtures cured at 80 °C or 35 °C (not included in Figure 4) showed similar behavior of the neat UP indicating no macroscopic phase separation. The last results can be thermodynamically explained taken into account the increase of Gibbs free energy as a consequence of reduction of the entropy of mixing during crosslinking process and that these systems have exothermic enthalpy of mixing (LCST behavior). This phenomenon has been studied by a few research groups [5,6,7].

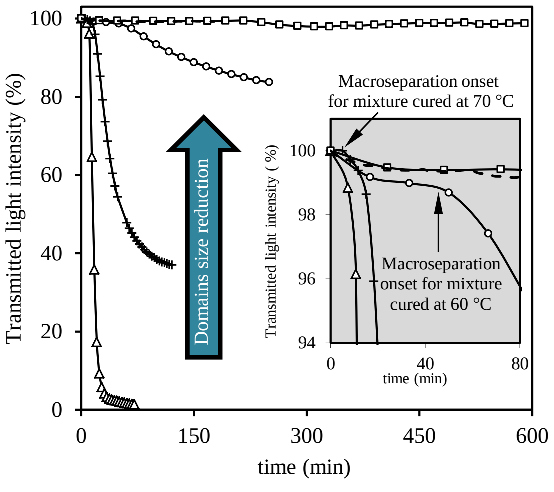

Figure 4. Transmitted light intensity as a function of curing time for (- - -) neat UP resin cured at 80 °C and for 25%EPE20 mixture cured at: (-Δ-) 80 °C, (-+-) 70 °C, (-o-) 60 °C and (-□-) 35 °C. The inset shows a magnification in time and transmitted light intensity range.

Miscibility. After curing at 80 °C, 5%EPE20, 5%EPE75 and 15%EPE75 mixtures remained transparent. On the contrary, 15%EPE20 was opaque. The miscibility of these cured mixtures from 25 to 230 °C and from -90 to 70 °C was analyzed by means of DMA and DSC, respectively

[3]. These measures permitted to observe two different T_gs in each cured mixture; one T_g with similar value of T_g of the neat BCPs (-58 °C for EPE75 and -63 °C for EPE20) and the other T_g with a value approximately the same of the T_g of the neat UP matrix (c.a. 165 °C).

Morphology. AFM images of Figure 5 depicted the morphology of neat UP resin and UP/EPE75 and UP/EPE20 mixtures with 5 wt % modifier cured at 80 °C. Figure 5b-c shows a sphere-like structure owing to the microphase separation of BCPs. Considering the DSC and DLS results for nonreactive mixtures, it can be concluded that the morphology of 5%EPE75 and 5%EPE20 cured mixtures were driven by PIPS and self-assembly mechanism, respectively [3]. Moreover, an evolution from sphere-like to worm-like phase separated domains varying the BCPs content was observed (images not included here).

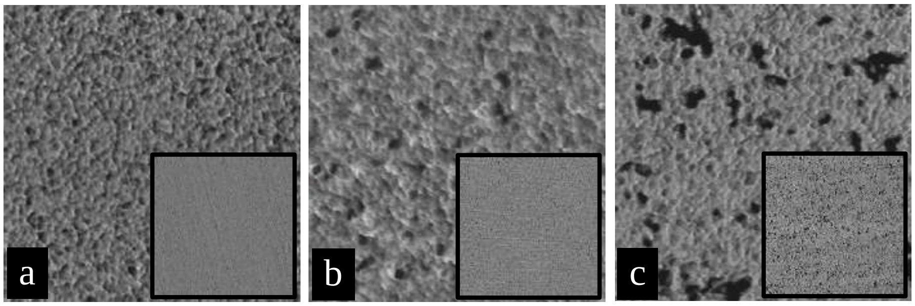

Figure 5. AFM images (0.5 µm x 0.5 µm) of (a) neat UP, (b) 5%EPE75 and (c) 5%EPE20 cured at 80 °C. The insets correspond to 3 µm x 3 µm AFM images.

Transparency. In order to examine the effects of the modifiers content on the optical transparency, UV-vis measurements at wavelengths from 300 to 800 nm were performed. Figure 6 shows regular light transmittance of UV-vis spectra and the visual appearance for neat UP resin, UP/EPE75 and UP/EPE20 cured mixtures.

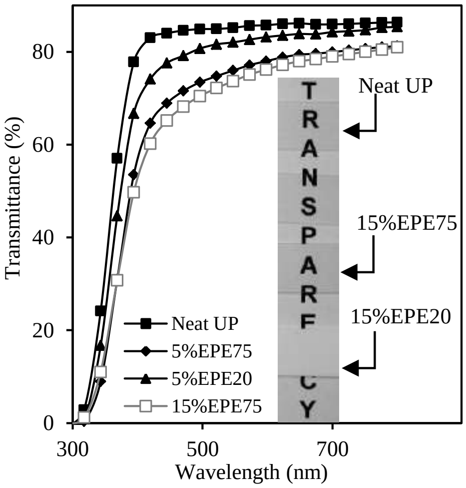

Figure 6. Transmittance in UV-vis spectra for (-■-) UP, (-♦-) 5%EPE75, (-▲-) 5%EPE20 and (-□-) 15%EPE75 mixtures. The inset corresponds to the digital image of sheets of cured mixtures of 1 mm thickness.

The visual appearance (see the inset of Figure 6) agrees with the UV-vis light transmittance measurements. As expected, an increase of BCPs content decreased the light transmittance. It was observed that transparency of UP/EPE75 cured mixtures was almost constant with varying EPE75 content. On the other hand, the transparency of UP/EPE20 cured mixtures was strongly depend on EPE20 content. This phenomenon can be explained considering that the light extinction through the thermosetting sheets occurs by matter absorption and the scattering due to heterogeneities or/and refractive index fluctuations [5,8].

*Mechanical properties***.** Flexural modulus (E) and critical the stress intensity factor (K_{Ic}) were measured to investigate the mechanical properties of the thermosetting mixtures. In general, a decrease in E with increasing BCPs content was observed. This fact can be directly related to the lower modulus of the BCPs incorporated to the UP matrix. The value of E for 5%EPE75 was lower than the measured for 5%EPE20 mixture (4.4, 3.3 and 3.6 GPa for neat UP, 5%EPE75 and 5%EPE20, respectively). However, the 15%EPE20 mixture showed the lower value of E (1.88 GPa) and the bigger domains (i.e. macrophase separation). Regarding the fracture toughness, all the mixtures exhibited an increase of K_{Ic}. The higher value of K_{Ic} was observed for 5%EPE20 mixture suggesting that the higher molecular weight of PPO central block was favorable to the fracture toughness. Indeed, in the case of 5%EPE20 mixture an improvement of K_{Ic} higher that 70 % was observed (0.44 and 0.67 MPa $m^{0.5}$ for neat UP and 5%EPE20 mixture, respectively). These results agree with the obtained morphology (see Figure 5) and the dependence of dispersion, size, and shape of the microstructure on toughness of the cured mixtures reported in the literature [2,9]. Toughening UP thermosetting modified with BCP have been reported elsewhere [4,10].

4. CONCLUSIONS

Two PEO-*b*-PPO-*b*-PEO block copolymers were used as modifiers for UP resin to fabricate nanostructured thermosetting materials. Novel results about the effect of curing temperature on morphology and optical properties were developed. It was found that PPO central block lead to a self-assembly or a PIPS that drive the nanostructuration of the matrix. Toughened UP thermosets were successfully achieved at higher values in UP/EPE20 mixtures.

5. ACKNOWLEDGEMENTS

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