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Comparison of morphologies and mechanical properties of crosslinked epoxies modified by polystyrene and poly(methyl methacrylate)) or by the corresponding block copolymer polystyrene-*b*-poly(methyl methacrylate)

I.A. Zucchi, M.J. Galante, R.J.J. Williams*

Institute of Materials Science and Technology (INTEMA), University of Mar del Plata and National Research Council (CONICET), Av. J.B. Justo 4302, 7600 Mar del Plata, Argentina

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Abstract

Polystyrene (PS, $M_n=28{,}400$, $PI=1.07$), poly(methyl methacrylate) (PMMA, $M_n=88{,}600$, $PI=1.03$), and PS (50,000)-*b*-PMMA (54,000) ($PI=1.04$), were used as modifiers of an epoxy formulation based on diglycidyl ether of bisphenol A (DGEBA) and *m*-xylylene diamine (MXDA). Both PS and PMMA were initially miscible in the stoichiometric mixture of DGEBA and MXDA at 80 °C, but were phase separated in the course of polymerization. Solutions containing 5 wt% of each one of both linear polymers exhibited a double phase separation. A PS-rich phase was segregated at a conversion close to 0.02 and a PMMA rich phase was phase separated at a conversion close to 0.2. Final morphologies, observed by scanning electron microscopy (SEM), consisted on a separate dispersion of PS and PMMA domains. A completely different morphology was observed when employing 10 wt% of PS-*b*-PMMA as modifier. PS blocks with $M_n=50{,}000$ were not soluble in the initial formulation. However, they were dispersed as micelles stabilized by the miscible PMMA blocks, leading to a transparent solution up to the conversion where PMMA blocks began to phase separate. A coalescence of the micellar structure into a continuous thermoplastic phase percolating the epoxy matrix was observed. The elastic modulus and yield stress of the cured blend modified by both PS and PMMA were 2.64 GPa and 97.2 MPa, respectively. For the blend modified by an equivalent amount of block copolymer these values were reduced to 2.14 GPa and 90.0 MPa. Therefore, using a block copolymer instead of the mixture of individual homopolymers and selecting an appropriate epoxy-amine formulation to provoke phase separation of the miscible block well before gelation, enables to transform a micellar structure into a bicontinuous thermoplastic/thermoset structure that exhibits the desired decrease in yield stress necessary for toughening purposes.

Keywords: Epoxies; Block copolymers; Blends

1. Introduction

Ternary blends consisting of two linear polymers dissolved in thermoset precursors may exhibit a double phase separation induced by polymerization [1,2]. This is particularly the case of blends of polystyrene (PS), poly(methyl methacrylate) (PMMA) and epoxy precursors. A thermodynamic analysis of these blends showed that a PS-rich phase was formed first while a PMMA-rich phase was segregated at more advanced conversions [1]. The epoxy matrix, PS and PMMA were present in three different phases in the cured blend. Morphologies generated in these systems could be varied by small additions of the block copolymer formed by the corresponding linear polymers (PS-*b*-PMMA) [2].

In this study, morphologies and mechanical properties of PS-PMMA-epoxy blends obtained either by using a mixture of the individual linear polymers (PS and PMMA) or the corresponding block copolymer (PS-*b*-PMMA), keeping constant the overall composition, will be compared. Micellar structure and mechanical properties of block copolymer-modified epoxies in the dilute limit, have been discussed in the literature [3]. Spherical micelles and vesicles were generated in blends containing epoxy and symmetric or asymmetric poly(ethylene oxide)–poly(ethylene-*alt*-propylene)

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* Corresponding author. Tel.: +54 223 481 6600; fax: +54 223 481 0046.

E-mail address: williams@fi.mdp.edu.ar (R.J.J. Williams).

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(PEO–PEP) block copolymer, with PEO volume fractions of 0.5 and 0.26, respectively. Due to the fact that PEO remained miscible up to high conversions, the micellar structure was preserved in the cured blends. In the present study, the epoxy-amine formulation was selected in order to produce phase separation of PMMA at conversions well before gelation. This should lead to coalescence of the micellar structure generating different morphologies than those obtained by using a mixture of PS and PMMA. The analysis of morphologies and mechanical properties of both types of modified-epoxies is the aim of the present study.

Table 1
Weight percents of linear polymers in epoxy-amine formulations

Denomination	wt% PS	wt% PMMA	wt% PS-*b*-PMMA (BC)
PS-E	10	0	0
PS-E (with BC)	9.5	0	0.5
PMMA-E	0	10	0
PMMA-E (with BC)	0	9.5	0.5
PS-PMMA-E	5	5	0
PS-PMMA-E (with BC)	4.75	4.75	0.5
BC-E	0	0	10

2. Experimental

2.1. Materials

The epoxy monomer was based on diglycidylether of bisphenol A (DGEBA, Der 332 Dow), with an epoxy equivalent of 348.5 g mol^{-1}. The hardener was *m*-xylylenediamine (MXDA, Aldrich), used in a stoichiometric proportion. Structures of both co-monomers are shown in Fig. 1.

Polystyrene (PS, $M_n=28{,}400$, $PI=1.07$), poly(methyl methacrylate) (PMMA, $M_n=88{,}600$, $PI=1.03$), and the block copolymer PS (50,000)-*b*-PMMA (54,000) ($PI=1.04$), were all from Polymer Source.

2.2. Formulations and cure procedure

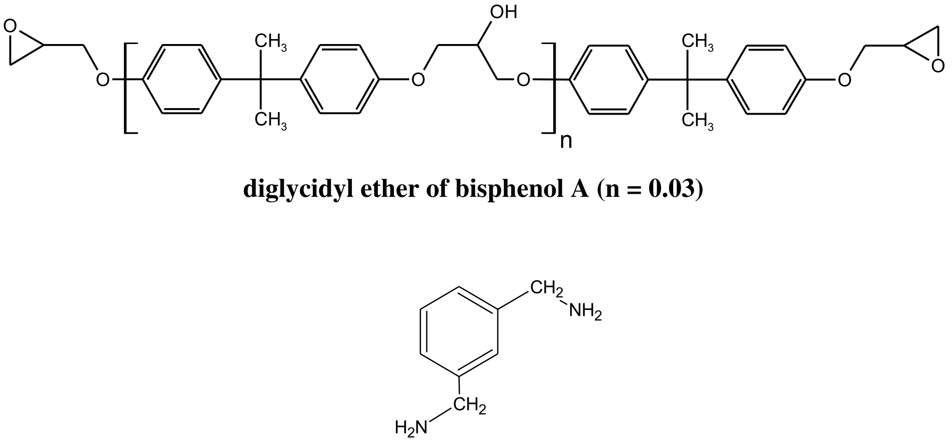
Compositions of different blends analyzed in this study are shown in Table 1 (E represents the epoxy-amine matrix and BC the block copolymer). PS-E and PMMA-E were studied as a reference of blends containing both linear polymers. PS-PMMA-E and BC-E blends contain similar amounts of PS and PMMA. Blends containing small amounts of BC as modifier were prepared for comparison purposes.

Appropriate amounts of modifiers were dissolved in DGEBA at about 80 °C until a transparent solution was obtained. Then, solutions were cooled to room temperature and the stoichiometric amount of MXDA was added. The cure was performed at 80 °C during 1 h. Phase separation and gelation occurred during this period. The polymerization was finally arrested by vitrification of the epoxy-rich phase. A post-cure at 130 °C during 30 min was carried out to attain complete conversion. Morphologies and mechanical properties of fully cured samples were analyzed.

2.3. Techniques

Differential scanning calorimetry (DSC, Pyris 1, Perkin–Elmer), was used to determine the glass transition temperature (T_g) of the fully-cured DGEBA-MXDA formulation, during a heating ramp at 10 °C/min under nitrogen.

Near-infrared spectroscopy (NIR) was used to determine the conversion vs. time curve at 80 °C, for the neat epoxy-amine formulation. A Genesis II FTIR device (Mattson), equipped with a heated transmission cell (HT-32, Spectra Tech) with quartz windows (32 mm diameter, 0.5 mm lead spacer) and a programmable temperature controller (Omega, Spectra Tech, $\Delta T=\pm 1$ °C), was employed. The



diglycidyl ether of bisphenol A (n = 0.03)

m-xylylenediamine

Fig. 1. Chemical structures of DGEBA and MXDA.

conversion of epoxy groups was followed by measuring the height of the absorption band at 4530 cm^{-1} with respect to the height of a reference band at 4620 cm^{-1} [4,5].

Transmission optical microscopy (TOM) was employed to determine cloud-point times of modified epoxy-amine formulations during polymerization at 80 °C. A Leica DMLB microscope equipped with a hot stage (Linkam THMS 600) and a photodetector incorporated into the optical path of the microscope, were used for this purpose.

Fracture surfaces of fully-cured blends obtained at room temperature, were coated with a fine gold layer and observed by scanning electron microscopy (SEM, Jeol JXA-8600 and Jeol 6460).

The elastic modulus (E) and yield stress (σ_Y) of fully-cured blends were determined at 20 °C from uniaxial compression tests. An Instron 4467 universal testing machine was used. Tests were performed at 2 mm min^{-1} with cylindrical specimens (length = 11 mm, diameter = 6.7 mm) machined out from cylinders of 40 mm length and the same diameter. Three to five specimens were used for every formulation.

3. Results and discussion

The neat DGEBA-MXDA system was first studied in order to define an appropriate cure cycle. Fig. 2 shows the conversion of epoxy groups as a function of time at 80 °C for the neat DGEBA-MXDA system. After 35 min of reaction the conversion increased at a very slow rate indicating that vitrification occurred at the polymerization temperature. The maximum conversion was close to 0.88. Samples cured for 1 h at 80 °C were postcured during 30 min at 130 °C. DSC scans of these samples showed a $T_g = 120$ °C (onset value) and no residual reaction heat. Therefore, fully converted samples could be obtained by the selected cure schedule.

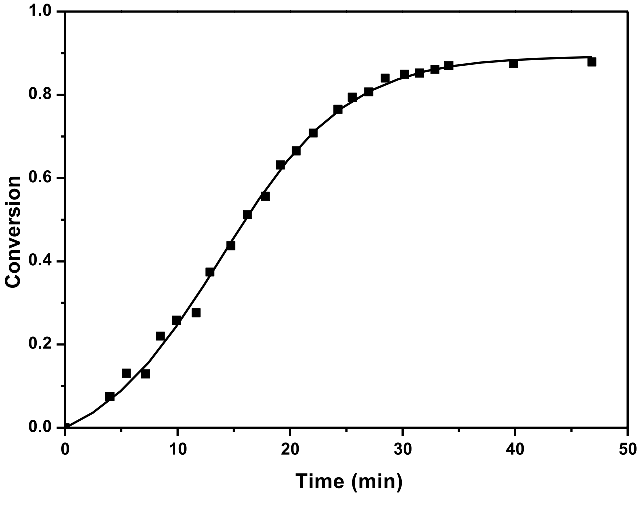


Fig. 2. Conversion of epoxy groups as a function of time for DGEBA-MXDA at 80 °C.

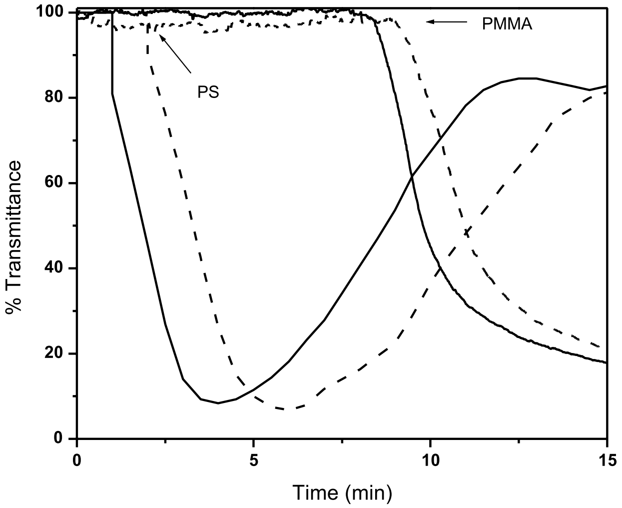


Fig. 3. Optical transmittance of PS-E and PMMA blends (continuous curves) and PS-E (with BC) and PMMA-E (with BC) blends (dashed curves), during polymerization at 80 °C.

The addition of 10 wt% modifier to the DGEBA-MXDA formulation retards the initial polymerization rate due to a dilution effect. After phase separation the situation becomes more complicated due to the partition of both monomers among the different phases. However, for a 10 wt% modifier the shift of the overall conversion curve could not be detected within the experimental error of the NIR technique. Therefore, the kinetic curve shown in Fig. 2 was used to estimate cloud-point conversions from the experimental values of cloud-point times.

Fig. 3 shows the variation of the optical transmittance of PS-E and PMMA-E blends, depicted with continuous curves, and PS-E (with BC) and PMMA-E (with BC), indicated with dashed curves, during a polymerization reaction at 80 °C. Every blend was homogeneous at the start of polymerization but blends containing PS were very close to the solubility limit. For these blends, a slight increase in conversion produced a sharp decrease in transmittance due to the phase separation of a PS-rich phase. In fact, the M_n of the PS was selected performing preliminary solubility tests in the mixture of monomers, at 80 °C. A small increase in M_n did not allow obtaining homogeneous solutions before the start of polymerization.

The addition of a small amount of PS-*b*-PMMA is expected to reduce the initial size of phase separated domains due to its emulsifying effect (increase in the concentration of particles and decrease in their average size). The small increase of the cloud-point conversion observed for the blend containing the block copolymer may be explained by the extra time needed to increase the size of dispersed domains to the range where they could be detected by visible light. For both blends containing PS a continuous increase in transmittance was detected at higher conversions. A similar phenomenon was observed for other PS-epoxy blends and explained by the continuous increase of

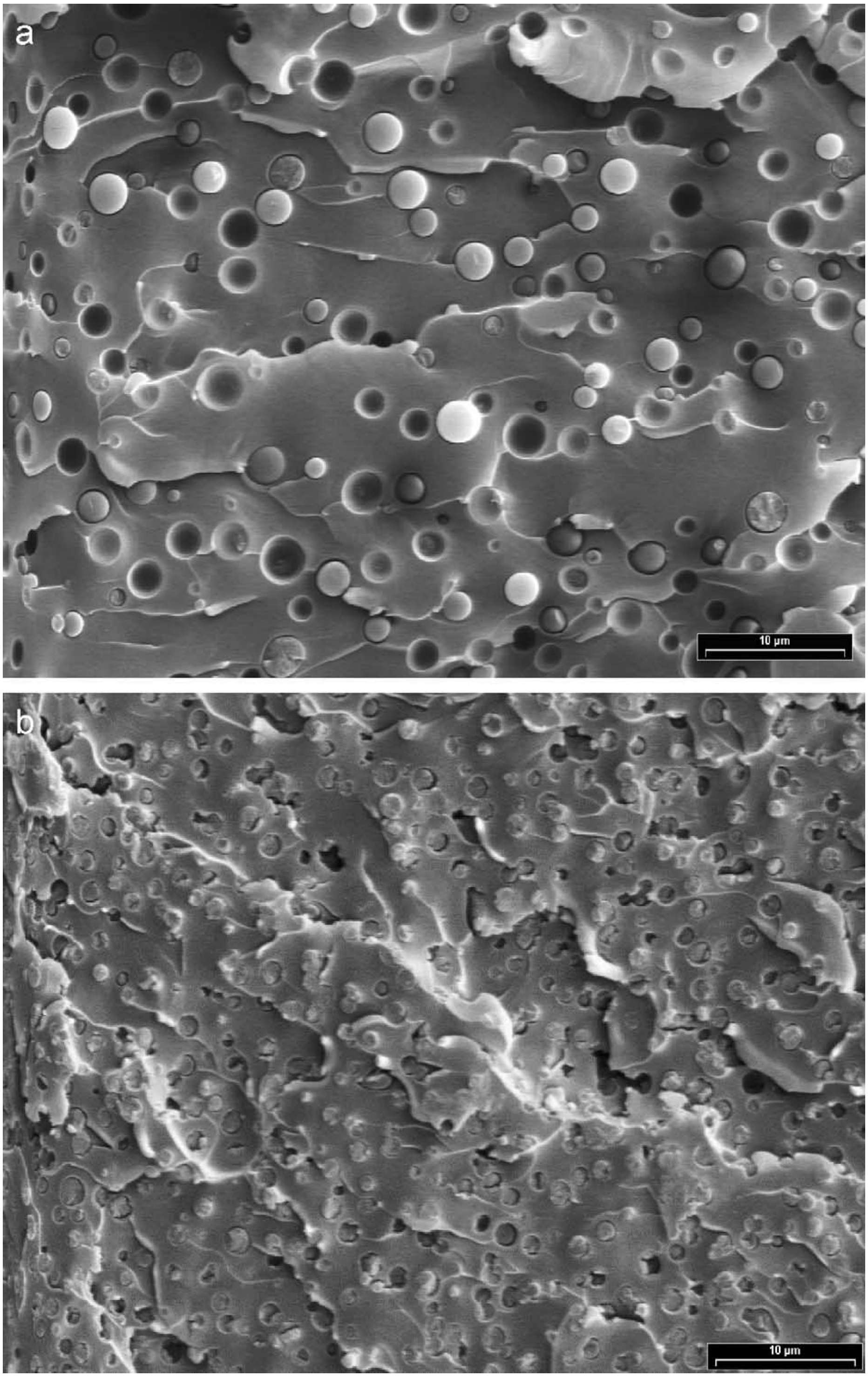


Fig. 4. SEM micrographs of PS-E blends: (a) without BC, (b) with BC.

the refractive index of the thermosetting polymer with conversion, matching the one of PS [2,6]. At full conversion, PS-E and PS-E (with BC) blends were transparent.

Phase separation in PMMA-E and PMMA-E (with BC) blends occurred at a conversion close to 0.2. Again, the addition of a small amount of block copolymer retarded the detection of the cloud point. For these blends the optical transmittance decreased continuously with conversion due to the increase in the volume fraction of dispersed phase exhibiting a different refractive index than that of the matrix.

A thermodynamic analysis of the phase separation process shows that there is a continuous evolution in the

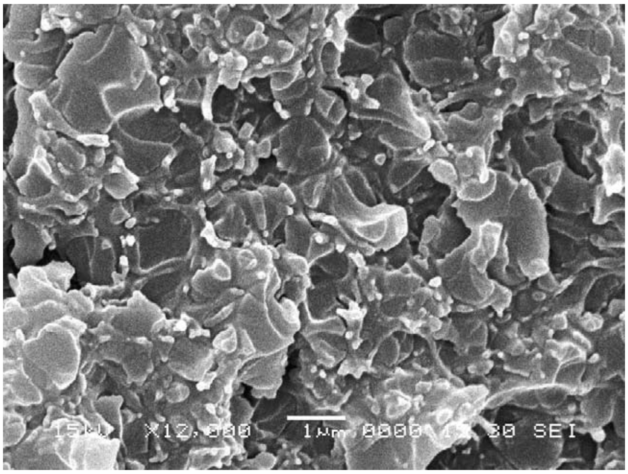


Fig. 5. SEM micrograph of a PMMA-E (with BC) blend.

composition of phases generated at the cloud-point [1,7]. As conversion increases one phase gets richer in the epoxy-amine polymer and the other in the thermoplastic. Eventually, the thermoplastic-rich phase may vitrify at the polymerization temperature fixing its morphology.

Fig. 4 shows SEM micrographs of PS-E and PS-E (with BC) blends. The average size of PS particles in PS-E blends is 1.7 ± 0.6 μm. The addition of a small amount of PS-*b*-PMMA enabled to reduce both the average size and the standard deviation of the particle distribution to 1.1 ± 0.3 μm. This confirms the emulsifying effect of the block copolymer placed at the boundary, with PS blocks located inside and PMMA blocks extending outside the particles. A close inspection of Fig. 4(b) reveals that the addition of the block copolymer produced a partial coalescence of particles. At the time of PMMA phase separation some of the PMMA blocks located in different particles may become part of a PMMA-rich domain driving the PS particles to which they are attached to coalescence. This is favored by the fact that PMMA phase separation occurs well before gelation of the epoxy-amine matrix (the ideal value of the gel conversion for an A_4+B_2 polycondensation is 0.577).

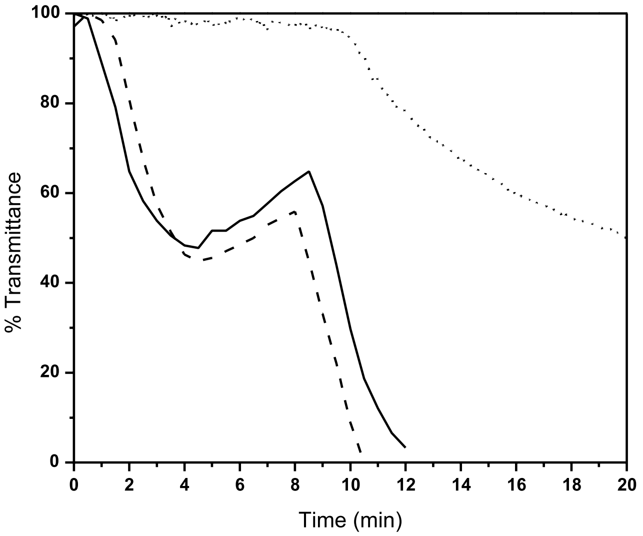


Fig. 6. Optical transmittance of PS-PMMA-E blends (continuous curve), PS-PMMA-E (with BC) blend (dashed curve), and BC-E blend (dotted curve), during polymerization at 80 °C.

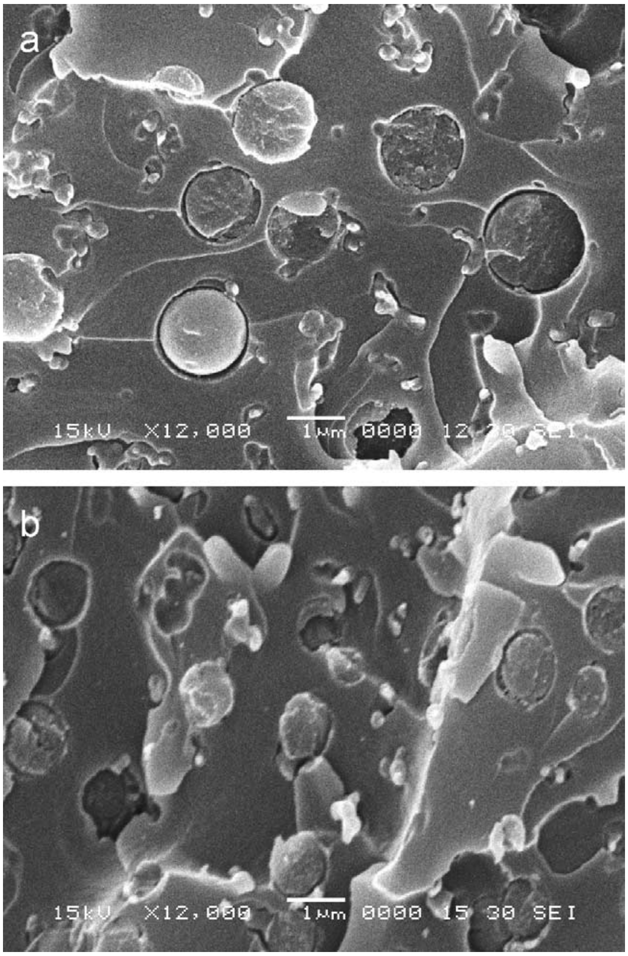


Fig. 7. SEM micrographs of PS-PMMA-E blends: (a) without BC, (b) with BC.

For PMMA-E and PMMA-E (with BC) blends, the average size of PMMA domains was relatively small. As an example, Fig. 5 shows a SEM micrograph of a PMMA-E (with BC) blend. White dispersed domains may be distinguished in the gray epoxy-amine matrix. Some of these small domains exhibit signs of plastic drawing. Their average size lies in the range of 0.1–0.2 μm.

Having identified cloud-point times and morphologies originated by the use of either PS or PMMA as a modifier of the epoxy-amine system, we can now analyze the phase separation process in blends where both linear polymers are present. Fig. 6 shows the optical transmittance of PS-PMMA-E blends (continuous curve), PS-PMMA-E (with BC) blend (dashed curve), and BC-E blend (dotted curve), during polymerization at 80 °C. A double phase separation process takes place in both PS-PMMA-E and

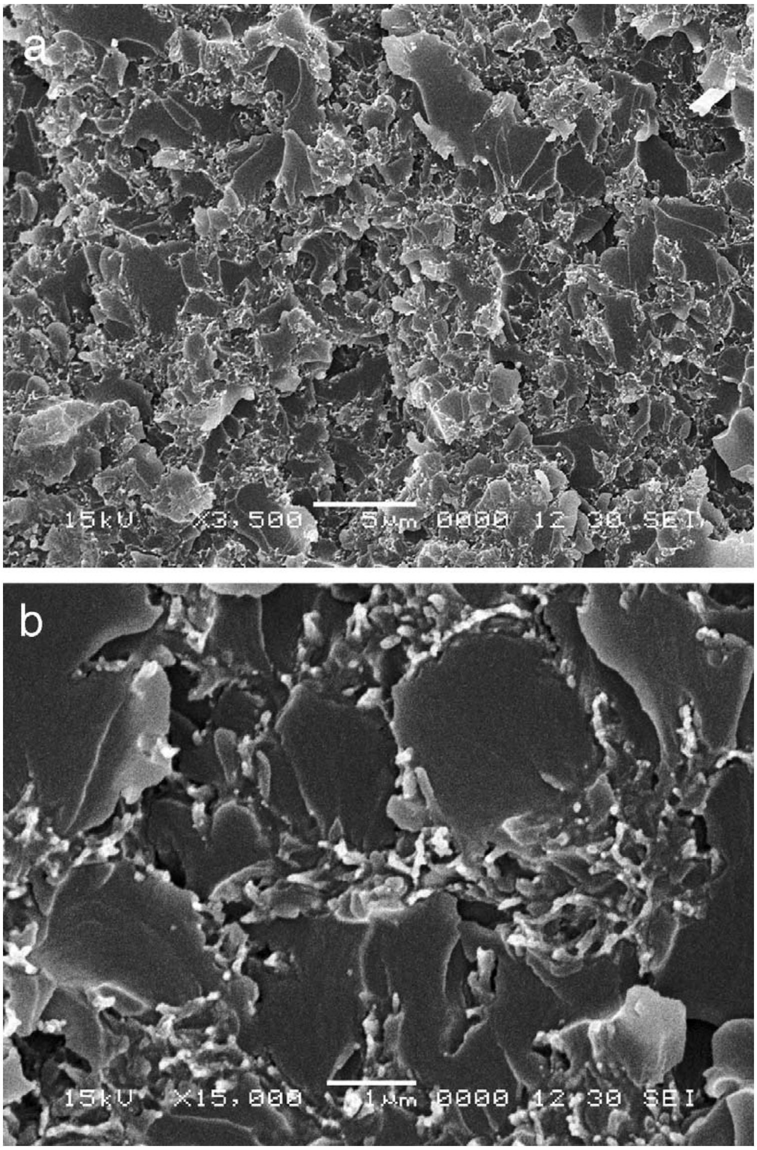


Fig. 8. SEM micrographs of BC-E blends.

PS-PMMA-E (with BC) blends as recorded by the two-step decrease of transmittance. Phase segregation of a PS-rich phase occurs at very low conversions, followed by the generation of the PMMA-rich phase at higher conversions. Both conversions are practically coincident with those determined for the blends containing either PS or PMMA as modifiers.

In the case of the BC-E blend, only the transmittance decrease assigned to the phase separation of the PMMA blocks, was observed. Blocks of PS with $M_n = 50,000$ were not miscible with the initial mixture of monomers at 80 °C. Spherical micelles with PS cores and PMMA arms are expected to be generated for a symmetric block copolymer with one block immiscible and the other miscible in the reactive solvent [3]. These disordered micellar dispersion does not scatter visible light due to the small size of the individual micelles. From the time when PMMA blocks becomes phase separated, a continuous decrease in transmittance was observed (Fig. 6). This is an indication of the coalescence of the micellar structure generating domains that scattered visible light.

Fig. 7 shows SEM micrographs of the PS-PMMA-E blend. This morphology was produced in two steps. First, the relatively large PS spheres were formed by polymerization-induced phase separation at low conversions. Then, the PMMA small domains were phase separated at a higher conversion but well before gelation. Some of these small domains are present at the boundary of PS spheres. The addition of a small amount of the block copolymer to the initial formulation led to some coalescence of PS spheres, generating some irregular-shape domains (Fig. 7(b)). This was due to the merging of PMMA blocks extending out of different particles, at the time of PMMA phase separation.

Table 2
Elastic modulus (E) and yield stress (σ_Y) of the neat epoxy matrix and different blends

Blend	E (GPa)	σ_Y (MPa)
Neat E	2.65±0.06	103.3±0.4
PS-E	2.54±0.01	97.1±1.2
PMMA-E	2.70±0.05	98.0±0.5
PS-PMMA-E	2.64±0.01	97.2±1.0
BC-E	2.14±0.02	90.0±1.8

As shown in Fig. 8, the morphology obtained for the BC-E blend was quite different than the other ones. A high dispersion of the thermoplastic phase in the epoxy matrix is observed, a morphology that resembles the filamentous structures reported in the literature when coalescence of a micellar structure takes place [8]. In the higher magnification micrograph (Fig. 8(b)), the thermoplastic phase seems to percolate through the matrix. Therefore, the morphology is characterized by the presence of bicontinuous phases, a fact which is highly desirable when the aim is to increase the fracture toughness of the thermoplastic/thermoset blend [9].

Values of the elastic modulus (E) and yield stress (σ_Y) of the neat epoxy matrix and different blends are shown in Table 2. Blends obtained by adding one of the linear polymers or a mixture of both linear polymers did not produce significant modifications of mechanical properties. The elastic modulus remained practically the same and the yield stress exhibited a small decrease. But the use of the block copolymer led to a significant decrease of both the elastic modulus and the yield stress, reflecting the fact that a completely different morphology was generated. Even if fracture tests were not carried out, the inverse correlation of the critical stress intensity factor, K_{IC}, with the yield stress [10,11], enables to assess that the bicontinuous morphology should provide an increase in the fracture resistance of the material.

4. Conclusions

Significantly different morphologies and mechanical properties were generated when replacing a mixture of two almost immiscible linear polymers (PS and PMMA) by the corresponding block copolymer (PS-*b*-PMMA), to modify an epoxy resin. The use of the mixture of the separate polymers imposes a strong limitation in both the size of the less miscible polymer (PS) and in the maximum mass fraction of both polymers, to obtain an initial homogeneous solution avoiding macroscopic phase separation. This is due to the mutual incompatibility between both linear polymers. Besides, generated morphologies consisting of three phases where both thermoplastics are present in different domains dispersed in the epoxy matrix do not produce a significant modification of mechanical properties with respect to those of the neat matrix. The use of the block copolymer enabled to remove these disadvantages while keeping the same overall composition of the final blend. Now there is no limitation in the size of the less miscible block or in the maximum fraction of the block copolymer to generate a nanostructure stabilized by the miscible block. In the dilute concentration regime, a micellar structure may be generated. Phase separation of the more miscible block induced by polymerization led to the generation of a bicontinuous thermoplastic/thermoset structure exhibiting the desired decrease in yield stress which is necessary for toughening purposes.

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