Transparent Multiphasic Polystyrene/Epoxy Blends

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Blends of polystyrene (PS) with an epoxy monomer (DGEBA) and a tertiary amine (BDMA), were initially miscible at 120°C but phase-separated at very low conversions in the course of polymerization. Although there was a significant difference between the refractive indices of polystyrene and the DGEBA/BDMA solution, the refractive index of the epoxy network increased in the course of polymerization, attaining a value close to that of PS at complete conversion. A sharp decrease of the light transmittance was observed at the cloud-point, observed at very low conversions. However, the continuous increase of the refractive index of the epoxy phase with conversion produced an approximate matching of both refractive indices, leading to transparent materials at complete conversion. Morphologies generated by reaction-induced phase separation depended on the molar mass distribution of polystyrene and its mass fraction in the blend. For a PS with a high value of the mass-average molar mass (M_w), it was possible to generate a dispersion of PS particles in the epoxy matrix (blends containing 5 wt% PS), phase-inverted morphologies (blends containing 15 wt% PS) and double-phase morphologies (blends with 10 wt% PS). Therefore, PS/DGEBA/BDMA blends could be used to obtain transparent epoxy coatings toughened by polystyrene particles or transparent polystyrene parts reinforced by a dispersion of epoxy particles.

INTRODUCTION

Thermoset-thermoplastic blends have gained increasing importance in recent years. A new material is generated with distinctive properties (thermal, mechanical, solvent resistance, etc.) to those of the pure polymers (1). In most cases these blends are prepared starting from a homogeneous solution of the thermoplastic polymer in the thermoset precursors and inducing phase separation during network formation (2). Depending on the initial ratio of both components, different structures may be obtained: thermoplastic domains dispersed in the thermoset matrix, bicontinuous morphologies or thermoset domains dispersed in a thermoplastic matrix. These blends are used for different purposes, e.g., to toughen the thermoset, to reinforce the thermoplastic or to reduce the processing temperature required for the pure thermoplastic.

The need to develop transparent multiphasic blends is known for several applications such as packaging or coatings. This is usually accomplished by matching the refractive indices of both phases, a method that is currently used for some thermoplastic blends. For the case of thermoplastic-modified epoxies there is not much information on possible multiphasic blends that satisfy the requirement of transparency. Kim *et al.* (3) described a blend based on triglycidyl *p*-aminophenol/ 4,4'-diaminodiphenylsulfone and poly(ether sulfone), exhibiting a perfect matching of refractive indices at full conversion of the epoxy resin. As the refractive index of the epoxy-rich phase increased continuously with conversion, at the cloud-point time the material

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was opaque due to the mismatch of refractive indices. However, at the end of cure the material became transparent. The aim of this paper is to show that a system based on diglycidylether of bisphenol A (DGEBA)/benzyldimethylamine (BDMA) and polystyrene (PS), exhibits a similar behavior. These formulations could be used to obtain transparent PS-modified epoxies or epoxy-reinforced polystyrenes.

EXPERIMENTAL

Materials

The epoxy monomer (DER 332, Dow), was based on diglycidylether of bisphenol A (DGEBA), with a mass per mol of epoxy groups equal to 174.3 g/mol. The tertiary amine used as initiator of the anionic polymerization was benzyldimethylamine (BDMA, Sigma), in an amount equal to 0.06 moles of BDMA per mol of epoxy groups.

Two commercial polystyrenes (PS) with very different polydispersity values were used. Average molar masses of one of them (PS1), were: $M_n = 57,400$ and $M_w = 96,000$, as determined by size exclusion chromatography (SEC). Corresponding values for the other one (PS2), were: $M_n = 39,800$ and $M_w = 297,000$.

PS/DGEBA blends were prepared at room temperature using methylene chloride as solvent. This was evaporated during 2 days at room temperature followed by several hours at 90°C, and cooling again to add the BDMA. Blends became turbid during the cooling step due to the phase separation of a PS-rich phase. However, heating to the cure temperature rendered these blends transparent again. Alternatively, blends containing up to 15 wt% PS1 were also prepared at 130°C without adding methylene chloride. Solutions were cooled and the corresponding amount of BDMA was added at room temperature. Blends prepared by both methods gave similar results.

Techniques

Transmission optical microscopy (TOM) was employed to determine cloud-point temperatures of PS/DGEBA blends, cloud-point times during polymerization, and the evolution of morphologies in the course of the phase separation process. A Leica DMLB microscope provided with a video camera (Leica DC 100) and a hot stage (Linkam THMS 600), was used for these purposes. Samples were placed between two glasses using a 0.5 mm stainless-steel spacer.

The polymerization kinetics was followed by differential scanning calorimetry (DSC, Perkin-Elmer Pyris 1), at 120°C, under a nitrogen atmosphere. Glass transition temperatures, defined at the mid-point of the change in specific heat, were determined during a subsequent scan at 10°C/min.

Phase separation during polymerization was followed recording the intensity of transmitted light by a glass cell containing the sample at constant temperature (4).

The index of refraction of the neat epoxy was measured with an Abbe's refractometer (Atago 1T), before polymerization (in the liquid state) and after complete cure (in the glassy state). For solid samples, the standard method for index of refraction of transparent organic plastics (ASTM D542-90), was used.

Plaques of the neat epoxy and PS/epoxy blends were obtained by casting the mixture into a mold consisting of two glass plates coated with siliconized paper and spaced by rubber cords of 2 mm diameter. Cure was carried out in an oven at T = 120°C for 4 h. Fracture surfaces of these plaques were coated with a fine gold layer and observed by scanning electron microscopy (SEM, Jeol JXA-8600).

RESULTS AND DISCUSSION

Cloud-Point Curves

The miscibility of both polystyrenes with the epoxy monomer was determined by TOM. An upper-critical-solution temperature (UCST) behavior was observed. Blends were heated to about 95°C to obtain homogeneous solutions, and were then cooled at 1°C/min to determine cloud-point temperatures. Experimental values did not change when the initial heating was performed to higher temperatures (up to 150°C), or when samples were kept at high temperatures during prolonged times (up to 2 h). Values were also checked by keeping the blends at temperatures $1-2$°C higher than the observed cloud-point temperatures to reassure that they remained homogeneous after several hours. *Figure 1* shows the experimental cloud-point curves for the PS/DGEBA blends as a function of the PS weight fraction. Each one of the blends was homogeneous above its cloud-point curve (UCST behavior).

The miscibility gap is particular sensitive to the weight-average and z-average of the distribution of molar masses (5). The PS with the largest value of M_w (PS2) was found to be less miscible than the other (PS1), as expected. The depression in the cloud-point curve of PS2 may be related to the existence of multiple critical points associated to multiphase equilibria (6). Such points may arise because of the asymmetry of the chain-length distribution, as is the case of PS2, and/or because of a strong concentration dependence of the interaction parameter (6).

When adding BDMA and heating beyond the cloud-point curve to obtain a homogeneous solution, there was a competition between the dissolution of PS and the advance in the polymerization reaction. Homogeneous solutions could be obtained in short times by heating the sample to temperatures in the range of 120°C. Therefore, the behavior of PS/epoxy blends was analyzed at this temperature.

Cure Kinetics

The neat epoxy and blends containing 5, 10 and 15 wt% PS2, were cured at 120°C in the DSC. The resulting thermograms (*Fig. 2*) show that the polymerization
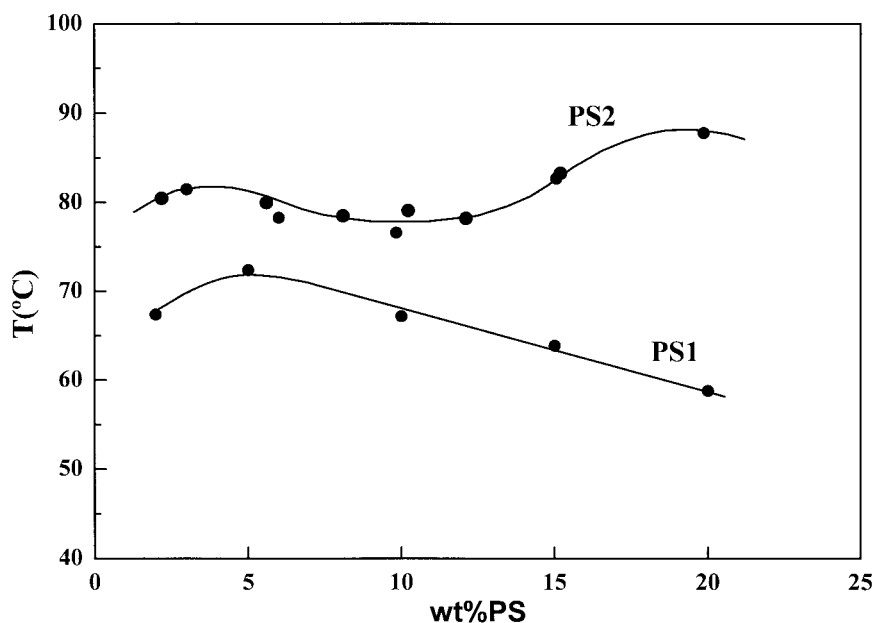
Fig. 1. *Cloud-point temperature as a function of the PS weight fraction for both PS/DGEBA blends (PS1: M_n = 57,400; M_w = 96,000; PS2: M_n = 39,800; M_w = 297,000).*

follows a typical autocatalytic course, due to the slow formation of the active species by the addition reaction of a tertiary amine to an epoxy group (7–13). A subsequent scan following the isothermal cure revealed the presence of two glass transition temperatures (T_g). Phase separation induced by polymerization led to an epoxy-rich phase with a T_g close to 80°C, and a PS-rich phase with a T_g close to 105°C.

Conversion vs. time curves were generated from DSC isothermal curves using partial reaction heats divided by the total reaction heat obtained in the same run. Results are shown in *Fig. 3* for the neat epoxy system and the blends with 5, 10 and 15 wt% PS2. The presence of PS has a clear retardation effect on the kinetics, particularly by prolonging the induction time necessary for the formation of active species. Studies of the BDMA-initiated polymerization of monoepoxies in solution (8), showed that the kinetics was affected by the nature of the solvent. The polymerization rate varied with the selected solvent in the
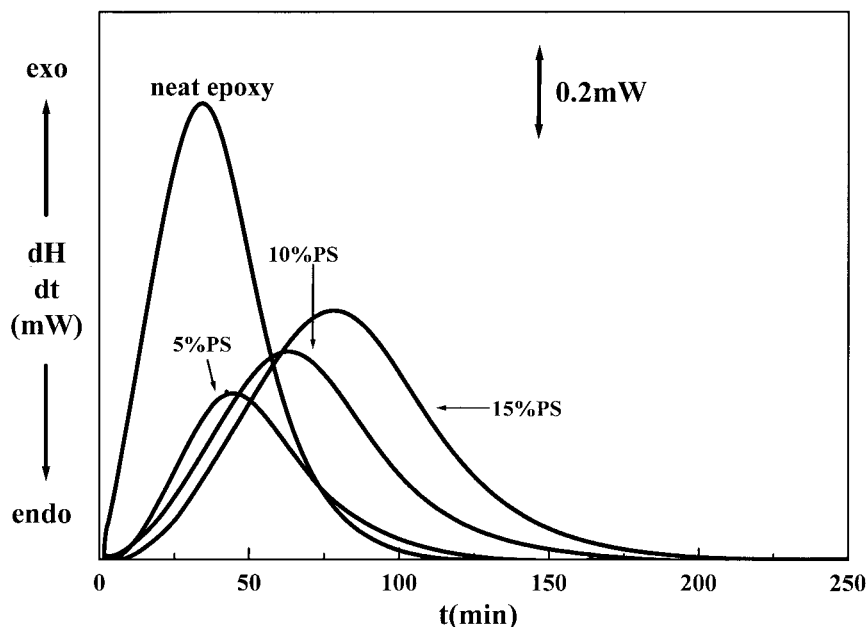

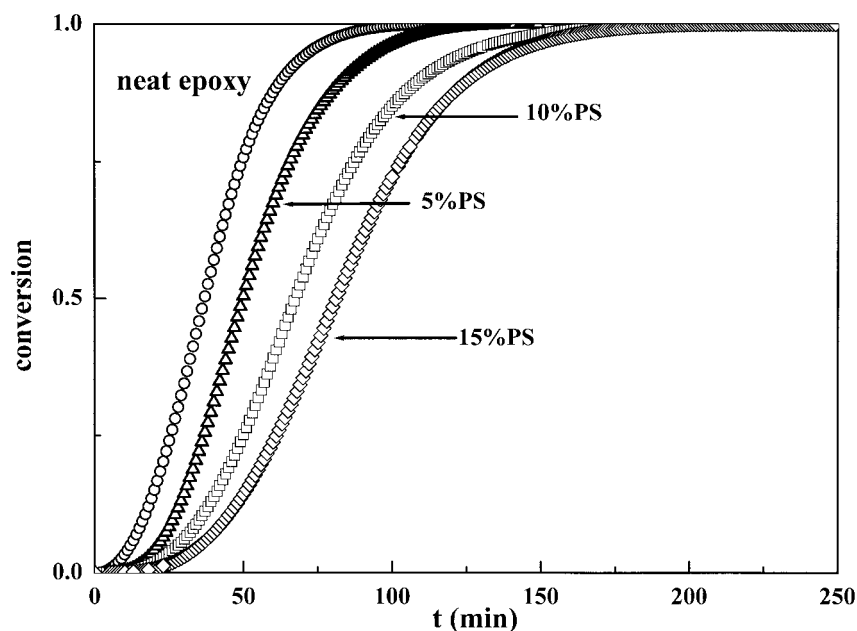Fig. 2. *DSC thermograms for the neat epoxy and blends containing 5, 10 and 15 wt% PS2, cured at 120°C.*

Fig. 3. Conversion vs. time curves for the neat epoxy and blends with 5, 10 and 15 wt% PS2 cured at 120°C.

following order: dimethylformamide > toluene > dioxane. The addition of PS modified the polarity of the reaction medium and produced a decrease in the rate of the anionic polymerization.

Phase Separation

Owing to the proximity of the cure temperature to the cloud-point curve of PS2, phase separation occurred at very low conversions. From cloud-point times determined by TOM, cloud-point conversions read from *Fig. 3*, were found to be lower than 0.05 for the three different compositions. In spite of a possible mismatch between thermal histories in DSC and TOM, affecting the conversion vs. time curves, it may be concluded that a very small advance in the polymerization reaction promoted phase separation of PS/epoxy blends.

The phase separation process was also followed using a light-transmission device. *Figure 4* shows the evolution of the intensity of the transmitted light for a PS/epoxy blend containing 8 wt% PS1, polymerized at 120°C. The cloud-point was characterized by a sharp decrease in the intensity of transmitted light at $t_{cp} = 38$ min. But soon after the cloud-point the intensity of transmitted light began to increase and, at the end of the cure, the blend exhibited a transparent aspect. A similar behavior was observed for every PS/epoxy blend prepared with PS1 or PS2, which appeared transparent at complete conversion.

In the course of polymerization the PS/epoxy blend changed from a transparent state (homogeneous solution before the cloud point), to an opaque state (heterogeneous system soon after the cloud point), and again to a transparent state (heterogeneous system at high conversions). This behavior may be explained by

the variation of the refractive index of the epoxy-rich phase during the cure. The refractive index of polystyrene is $n_{PS} = 1.590 - 1.592$, at 20°C (14). The refractive index of the epoxy monomer/tertiary amine formulation, measured at room temperature before cure, was $n_E(0) = 1.566$. The corresponding value for the completely cured epoxy, measured at room temperature, was $n_E(\infty) = 1.586$. Therefore, due to the low values of cloud-point conversions, the difference in the refractive indices of epoxy-rich and PS-rich phases was significant at the time of phase separation, leading to an opaque material. But this difference became very low towards the end of polymerization, leading to a transparent multiphasic blend. A similar phenomenon was reported for an epoxy-amine system modified with poly(ether sulfone) (3).

Morphologies

Morphologies generated in the course of the reaction-induced phase separation of a thermoplastic-thermoset blend, depend largely on the relative location of the initial thermoplastic concentration, $w_{TP}(0)$, with respect to the concentration of the critical point, $w_{TP}(crit)$ (1). For $w_{TP}(0) \ll w_{TP}(crit)$, the final morphology consists of a dispersion of thermoplastic-rich particles in a thermoset-rich matrix. For $w_{TP}(0) \gg w_{TP}(crit)$, a phase inverted structure is usually obtained, with thermoset-rich particles dispersed in a thermoplastic rich matrix. In a composition region close to the critical point, $w_{TP}(0) \sim w_{TP}(crit)$, a variety of morphologies may be developed: bicontinuous structures, double-phase morphologies (consisting of a conglomerate of two types of macroscopic domains: ones showing a dispersion of thermoplastic-rich particles and other ones exhibiting a phase-inverted structure), ribbonlike
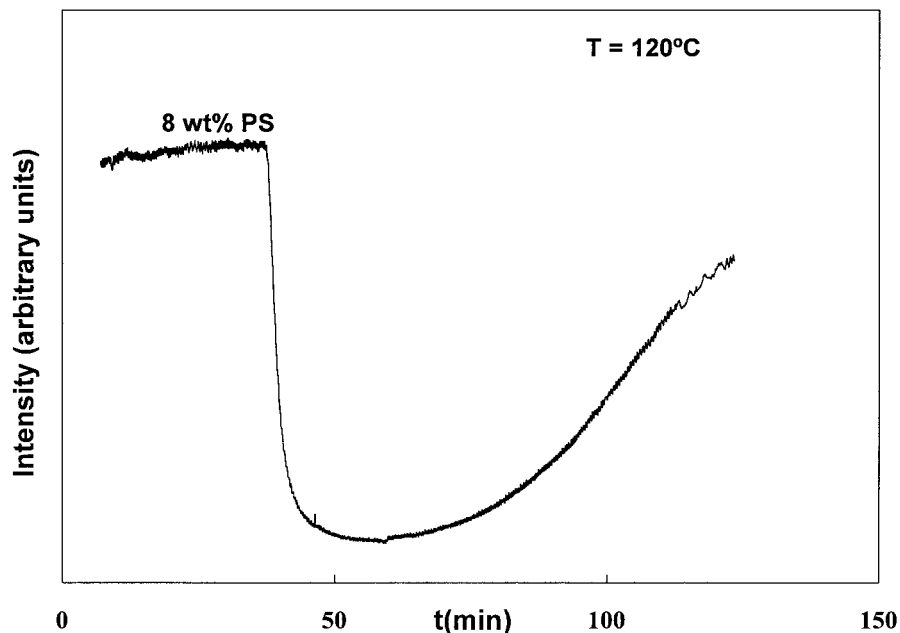
Fig. 4. *Evolution of the transmitted light during polymerization for a PS/epoxy blend with 8 wt% PS1, at 120°C.*

structures, etc. The situation may be much more complex in the case of the presence of multiple critical points leading to multiphase equilibria.

The location of the critical point depends on the value of M_w and M_z of both polymers and the third derivative of the interaction function with respect to composition (5). Increasing M_w and M_z shifts the location of the critical point to lower values of w_{TP}. This means that equal initial PS mass fractions in PS/epoxy blends, may lead to different morphologies depending on the values of M_w and M_z of the starting PS. Therefore, it may be expected that PS1 and PS2 lead to different morphologies at the same initial mass fraction of thermoplastic.

Final morphologies of PS/epoxy blends with 5, 10 and 15 wt% PS2, cured at 120°C, were analyzed using

SEM. *Figure 5* shows morphologies generated in blends containing 5 wt% PS2, at two different magnifications. A dispersion of PS particles with sizes in the range of $1-5$ μm, is observed. This is the usual morphology generated in the off-critical region of low thermoplastic concentrations.

For blends with 15 wt% PS2, a phase-inverted morphology typical of the off-critical region of high thermoplastic concentrations, was observed. *Figure 6* shows SEM micrographs for this case, at two different magnifications. Very large epoxy particles with sizes in the range of several hundreds micrometers, are embedded with a PS-rich phase exhibiting a secondary dispersion of smaller epoxy particles, with sizes in the range of $5-15$ μm. These samples were disintegrated after a few minutes immersion in methylene chloride
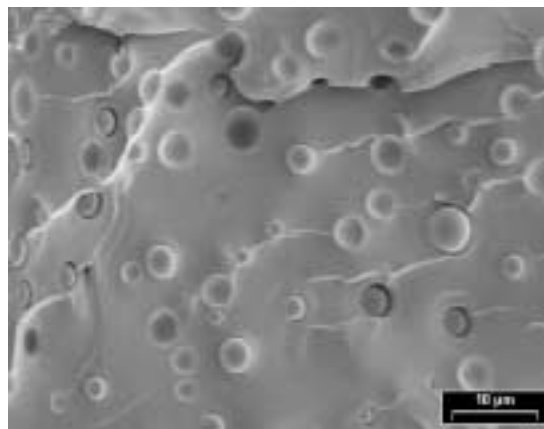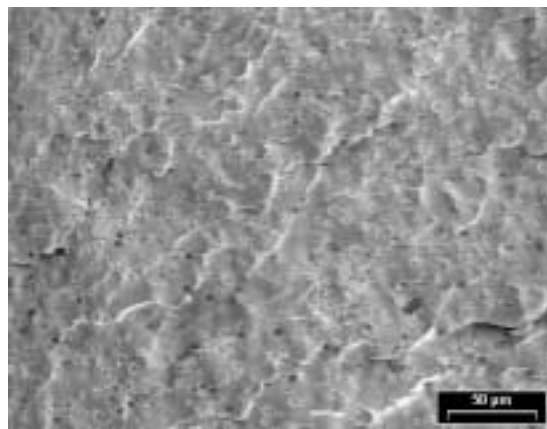

Fig. 5. *SEM micrographs of morphologies generated in a PS/epoxy blend with 5 wt% PS2, cured at 120°C, at two different magnifications.*
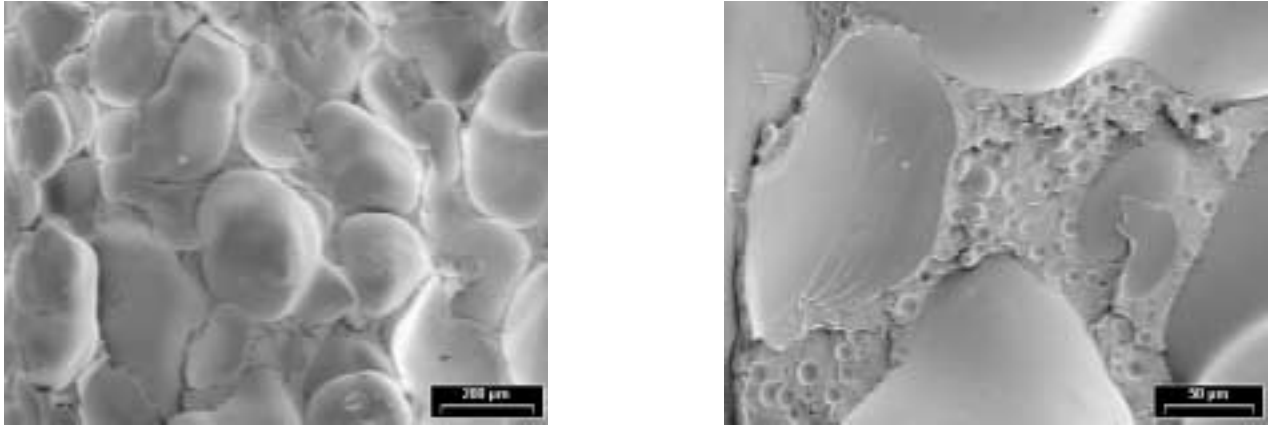
Fig. 6. SEM micrographs of morphologies generated in a PS/epoxy blend with 15 wt% PS2, cured at 120°C, at two different magnifications.

at room temperature. This proved that large epoxy particles were in fact embedded by PS and did not form a continuous structure.

The generation of the phase-inverted morphology was followed by TOM, during the cure at 120°C. *Figure 7* shows a sequence of TOM micrographs for the

PS/epoxy blend with 15 wt% PS2, taken in the same region of the sample. Micrograph a) shows the presence of a distribution of large spherical epoxy domains after 28 min polymerization (the view is a superposition of domains located in different depths). In micrograph b), taken at 34 min, the initially-formed
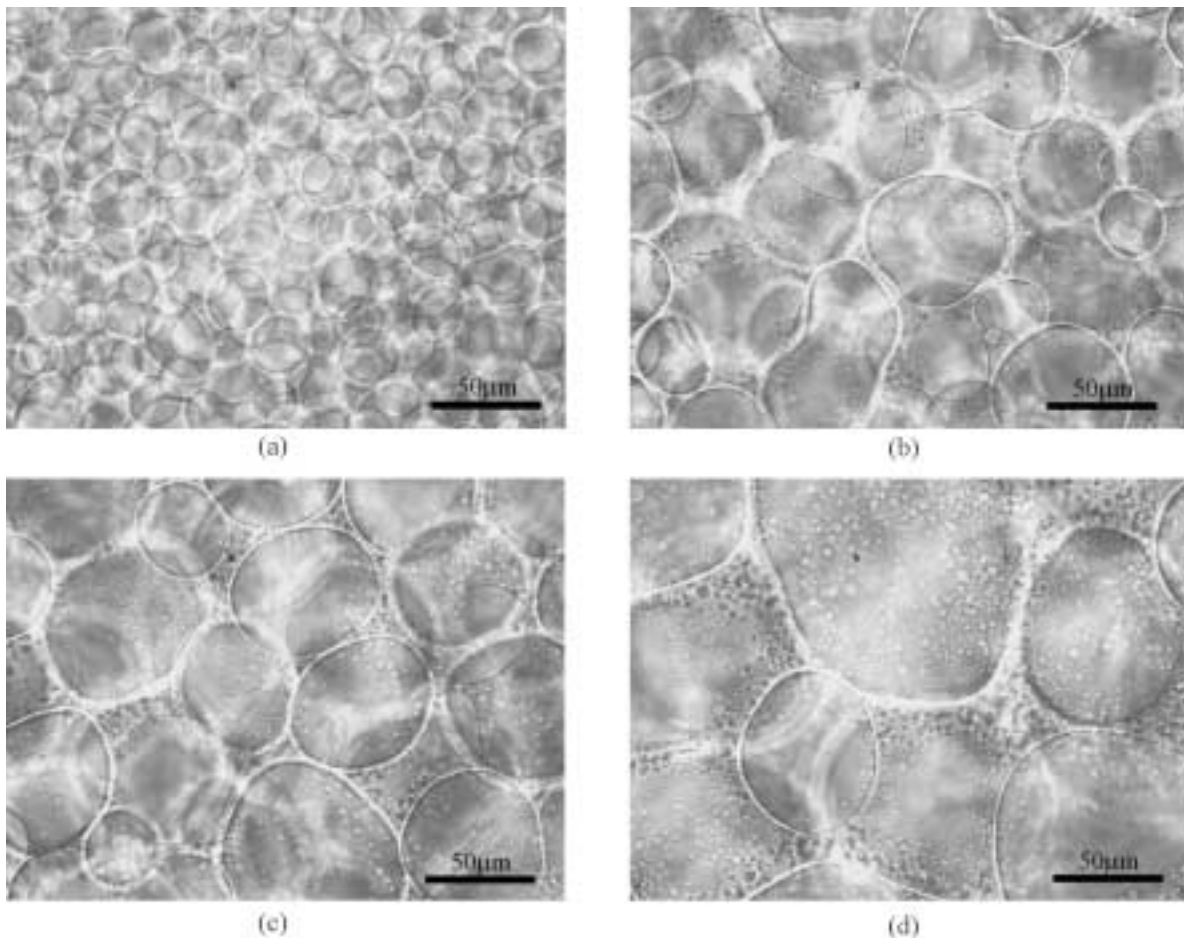

Fig. 7. Sequence of TOM micrographs taken in the course of the phase separation in a PS/epoxy blend with 15 wt% PS2, cured at 120°C; a) 28 min, b) 34 min, c) 37 min, d) 44 min.

domains exhibit irregular shapes and larger characteristic sizes, possibly produced by coalescence of the smaller domains. A secondary phase separation is evidenced in the PS-rich phase embedding the large epoxy domains. The occurrence of a secondary phase separation in the thermoplastic-rich phase, has been theoretically predicted and experimentally observed in several systems (1, 2, 15). This is because the PS-rich phase separated soon after the cloud point, contains a significant fraction of epoxy monomer and low molar-mass oligomers. As the polymerization continues in the PS-rich phase, epoxy domains are phase separated and, owing to the high viscosity of the PS matrix, they cannot merge with the large epoxy domains first generated. Micrographs c) and d), taken at 37 and 44 min, show the coalescence of primary particles and the growth of the secondary particles dispersed in the PS continuous phase. Micrograph d) resembles the final picture recorded in the SEM micrograph of this blend. The timescale for the development of a morphology resembling the final one, constitutes a small fraction of the timescale necessary to obtain full conversion.

For blends with 10 wt% PS2, morphologies generated were typical of compositions located close to the critical point. This is consistent with the depression in the cloud-point curve found in this range of compositions, shown in *Fig. 1*. This depression was identified with the location of a critical point (16), but the situation may be much more complicated due to the possible existence of multiple critical points (6). *Figure 8* shows morphologies generated for the PS/epoxy blend with 10 wt% PS2, cured at 120°C to complete conversion. A double-phase morphology was generated, consisting of the simultaneous presence of macroscopic domains exhibiting morphologies generated for both low and high PS concentrations. The macroscopic domain located at the right in *Fig. 8a* shows a dispersion of PS particles in an epoxy matrix (a magnification is presented in *Fig. 8b*). The macroscopic domain located at the left, exhibits the characteristic phase-inverted morphology (*Fig. 8c* shows a magnification of this region). The fracture surface shown in *Fig. 8a* reveals also the presence of the continuous PS phase embedding the large epoxy domains.

Morphologies generated for blends with PS1 consisted of a dispersion of PS particles in the epoxy matrix, for the three selected compositions (5, 10 and 15 wt% PS). This is the result of the shift of the critical point to higher thermoplastic concentrations. As an example, *Fig. 9* shows the resulting morphology for a blend with 10 wt% PS1, polymerized at 120°C. A dispersion of PS particles with diameters in the range of $2-10$ μm, is observed. This contrasts significantly with the double-phase morphology generated when using a similar mass fraction of PS2.
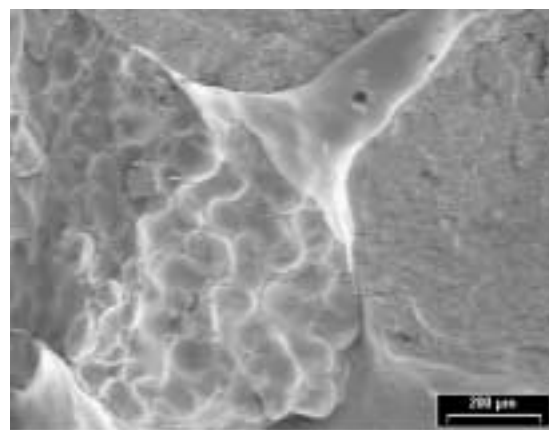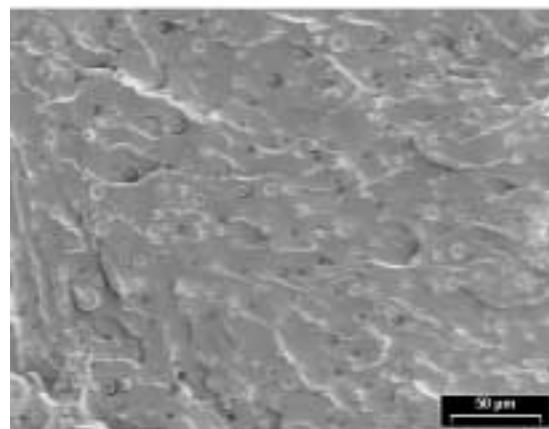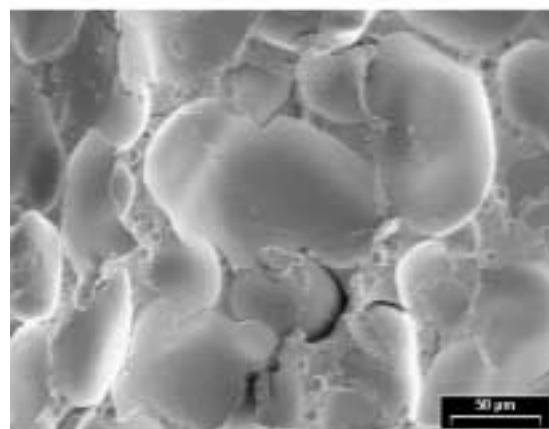
Fig. 8. *SEM micrographs of morphologies generated in a PS/epoxy blend with 10 wt% PS2, cured at 120°C; a) double-phase morphology, b) phase with a low PS concentration, c) phase with a high PS concentration.*
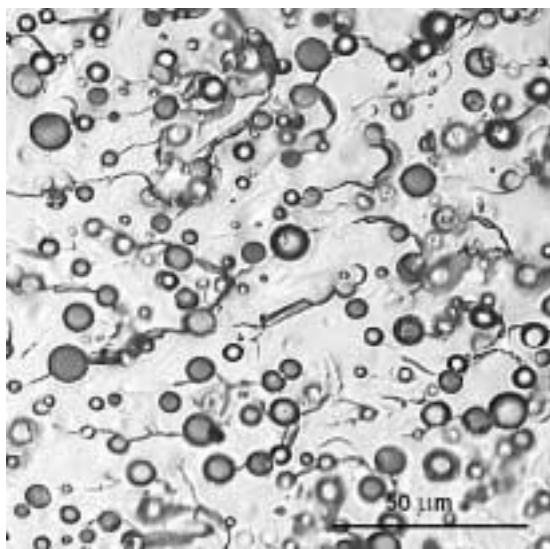
a dispersion of PS particles in the epoxy matrix (blends containing 5 wt% PS), phase-inverted morphologies (blends containing 15 wt% PS) and double-phase morphologies (blends with 10 wt% PS). Therefore, PS/DGEBA/BDMA blends could be used to obtain transparent epoxy coatings toughened by polystyrene particles or transparent polystyrene parts reinforced by a dispersion of epoxy particles.

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Fig. 9. TOM micrograph showing the morphology generated in a PS/epoxy blend with 10 wt% PS1, polymerized at 120°C.

CONCLUSIONS

Transparent multiphasic blends could be generated by reaction-induced phase separation of a polystyrene solution in DGEBA/BDMA. Although there was a significant difference between the refractive indices of polystyrene, $n_{PS} = 1.590-1.592$, and the DGEBA/BDMA solution at room temperature, $n_E(0) = 1.566$, the refractive index of the epoxy network increased in the course of polymerization attaining a value of $n_E(\infty) = 1.586$, at complete conversion. A sharp decrease of the light transmittance was observed at the cloud-point, observed at very low conversions. However, the continuous increase of the refractive index of the epoxy phase with conversion produced an approximate matching of both refractive indices, leading to transparent materials at complete conversion.

Morphologies generated by reaction-induced phase separation depended on the molar mass distribution of polystyrene and its mass fraction in the blend. For a PS with a high value of M_w, it was possible to generate