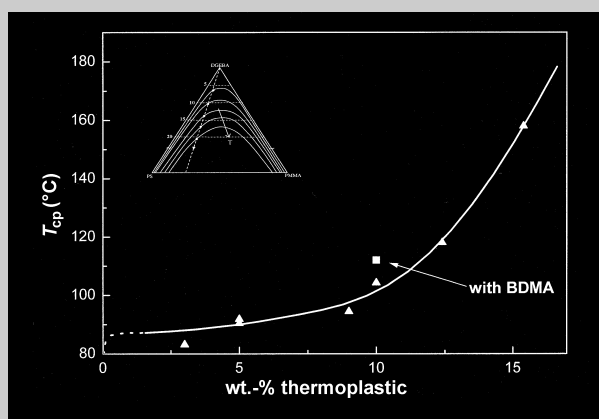**Full Paper:** Homogeneous solutions of polystyrene (PS) and poly(methyl methacrylate) (PMMA) in diglycidylether of bisphenol A, containing about 8 wt.-% total thermoplastic, and with or without 0.5 wt.-% of a PS-*b*-PMMA block copolymer, were polymerized in two ways (i) in the presence of a tertiary amine (benzyldimethylamine, BDMA), or (ii) using a stoichiometric amount of a diamine (4,4′-diaminodiphenyl sulfone, DDS). A double phase-separation was recorded by light transmission during polymerization. A PS-rich phase was separated at low conversions and a PMMA-rich phase was segregated at more advanced conversions. The addition of the block copolymer produced significant changes in the morphologies generated. For the BDMA-initiated polymerization, the presence of the block copolymer made the small PMMA-rich domains clearly discernible in transmission electron microscopy (TEM) micrographs. For the DDS-cured system, the addition of the block copolymer led to a dispersion of small PS-rich particles encapsulated by PMMA shells. The possibility of generating a stable dispersion of biphasic particles by polymerization-induced phase separation opens a new way to modify thermosetting polymers for toughening purposes.

Cloud-point curve for a PS/PMMA/DGEBA blend at a constant ratio of PS/PMMA = 75:25, as a function of the wt.-% of total thermoplastic in the formulation (an experimental point for a formulation containing BDMA is also shown). The one-phase region is located above the curve. The triangular diagram (insert) shows a qualitative representation of the miscibility region in ternary blends as a function of temperature.

Influence of the Addition of Polystyrene-*block*-poly(methyl methacrylate) Copolymer (PS-*b*-PMMA) on the Morphologies Generated by Reaction-Induced Phase Separation in PS/PMMA/Epoxy Blends

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Introduction

The possibility of producing a double phase-separation induced by polymerization in ternary blends of two different thermoplastics dissolved in an epoxy-amine reactive mixture, has been recently reported in the literature.[1] The two thermoplastics were monodisperse fractions of polystyrene (PS) and poly(methyl methacrylate) (PMMA), and the reactive solvent was a stoichiometric solution of diglycidylether of bisphenol A (DGEBA) and 4,4′-diaminodiphenyl sulfone (DDS). PS exhibited a lower solubility than PMMA in the reactive solvent; a PS-rich phase was segregated at low conversions while a PMMA-rich phase was separated at more advanced conversions. Morphologies generated consisted of a bimodal

dispersion of PS domains (large domains with sizes in the range 5–20 µm and small domains with sizes in the range 0.2–1 µm), together with a dispersion of PMMA-rich domains with sizes in the range 0.2–1.5 µm. Large PS domains were presumably formed by coalescence of the small particles, a process driven by the low viscosity of the solution at the conversion where PS was phase-separated.

The aim of this work was to examine the effect of adding a small amount of PS-*b*-PMMA (block copolymer) to the initial formulation on the morphologies generated by reaction-induced phase-separation in PS/PMMA/epoxy blends. Two different chemistries for the epoxy network formation will be explored: a) homopolymerization initiated by a tertiary amine (benzyldimethylamine, BDMA), and b) stepwise polymerization using a stoichiometric amount of a diamine (DDS). It will be shown that, by using an adequate selection of reaction conditions, a dispersion of biphasic particles consisting of PS-cores encapsulated by a PMMA-shell can be generated by reaction-induced phase separation. This may lead to a new generation of epoxy-modifiers for toughening purposes.

Experimental Part

Materials

An epoxy monomer based on DGEBA, was used. Two commercial products, MY790 (Ciba) and DER 332 (Dow), with the same epoxy equivalent weight (174 g · mol^{-1}), were employed. Both gave the same miscibility curves but different cure kinetics, possibly due to the different content of impurities acting as catalysts. DER 332 was the epoxy monomer used in reactive formulations with a tertiary amine or with a diamine.

The tertiary amine used as initiator of the anionic polymerization was BDMA (Sigma), in an amount of 0.06 moles of BDMA per mole of epoxy groups. The selected diamine (DDS, Fluka), was used in stoichiometric proportion with respect to DER 332.

Polydisperse PS and PMMA were used to obtain cloud-point curves of ternary blends, and to analyze phase-separation during the BDMA-initiated polymerization. Their average molar masses, PS ($\overline{M}_n = 57\,400$, $\overline{M}_w = 96\,000$), PMMA ($\overline{M}_n = 41\,400$, $\overline{M}_w = 80\,000$), were determined by size-exclusion chromatography using a universal calibration curve. Monodisperse PS and PMMA from Polymer Source, were used in ternary blends cured with DDS. Reported average molar masses were: PS ($\overline{M}_n = 88\,600$, $\overline{M}_w = 91\,000$), PMMA ($\overline{M}_n = 83\,000$, $\overline{M}_w = 86\,000$). The block copolymer used as an additive for both systems was poly(styrene-*b*-methyl methacrylate) from Polymer Source, $\overline{M}_n = $ PS (50\,000)-*b*-PMMA (54\,000), with $\overline{M}_w/\overline{M}_n = 1.04$.

PS/PMMA/DGEBA blends, with or without the extra addition of a specified amount of PS-*b*-PMMA, were prepared at 140 °C until the formation of a homogeneous solution. For blends cured in the presence of the tertiary amine, solutions were cooled to room temperature and the corresponding amount of BDMA was added. For blends cured with DDS, temperature was decreased to 135 °C when DDS was added with stirring until a homogeneous solution was obtained. For the determination of the cloud-point curves of ternary blends, where compositions were varied in a broader range, methylene chloride was used as a solvent at room temperature. It was evaporated over 2 d at room temperature followed by several hours at 80 °C.

Techniques

Transmission optical microscopy was employed to determine cloud-point temperatures of ternary blends. A Leica DMLB microscope provided with a video camera (Leica DC 100) and a hot-stage (Linkam THMS 600), was used for these purposes. Phase-separation during polymerization was followed by recording the intensity of transmitted light from a glass cell containing the sample at constant temperature.[2]

The evolution of dynamic mechanical spectra as a function of polymerization time at constant temperature was recorded using a Rheometrics dynamic analyzer (RSA II), in a frequency range between 1 and 100 rad · s^{-1}. Parallel-plate geometry was used (plate diameter = 25 mm).

TEM images of ultrathin sections of cured samples, were obtained using a JEM-200 CX device (Jeol), with an accelerating voltage of 80 kV. The distinction between PS-rich and PMMA-rich domains could be made by staining with RuO$_4$.[3] PMMA did not react with RuO$_4$ under the applied staining conditions and therefore appeared bright. PS was readily attacked and appeared dark while the epoxy matrix appeared gray. But, even without staining, PS and PMMA domains could be clearly distinguished in TEM micrographs.

Results and Discussion

Cloud-Point Curves of PS/PMMA/DGEBA Blends

Figure 1 shows the cloud-point curve for PS/DGEBA blends. An upper-critical-solution-temperature behavior (UCST) was observed (the one-phase region is located above the cloud-point curve). PMMA/DGEBA blends led to homogeneous solutions in all proportions.[4–6] The different miscibility of PS and PMMA with DGEBA, explains the fact that during the polymerization-induced phase-separation in PS/PMMA/DGEBA blends (including a hardener), a PS-rich phase was separated at lower conversions than a PMMA-rich phase.[1]

Figure 2 shows the cloud-point curve for a ternary PS/PMMA/DGEBA blend containing a constant ratio, PS/PMMA = 75:25. The one-phase region is located above the cloud-point curve (UCST behavior). The triangular diagram (insert) shows a qualitative representation of the miscibility of ternary blends in the region of high DGEBA concentrations. Blends with the selected PS/PMMA ratio are located along the dashed line. Coexistence curves for different temperatures are indicated (the one-phase region is located outside the curves). Increasing the thermoplastic wt.-% leads to an increase in the
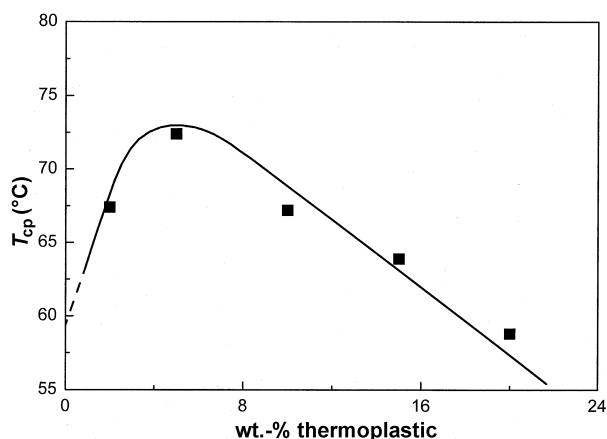
Figure 1.   Cloud-point curve of a PS-DGEBA binary blend with UCST behavior.
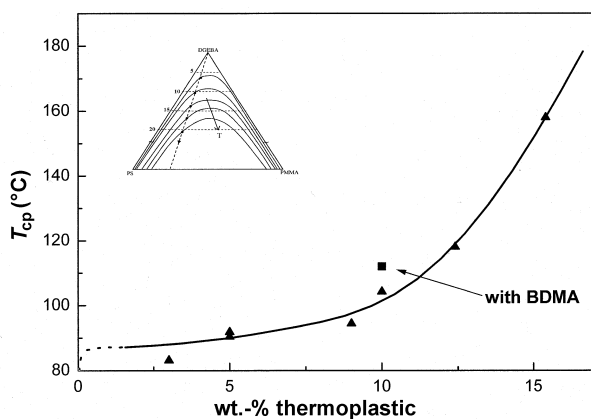

Figure 2.   Cloud-point curve for a PS/PMMA/DGEBA blend at a constant ratio of PS/PMMA = 75:25, as a function of the wt.-% of total thermoplastic in the formulation (an experimental point for a formulation containing BDMA is also shown). The one-phase region is located above the curve. The triangular diagram (insert) shows a qualitative representation of the miscibility region in ternary blends as a function of temperature.
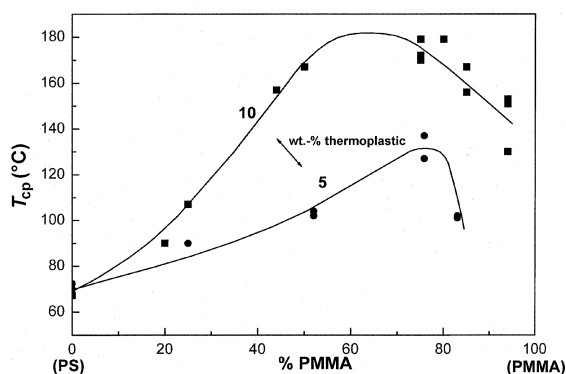

Figure 3.   Cloud-point curves of PS/PMMA/DGEBA blends containing 5 and 10 wt.-% of total thermoplastic, as a function of the relative fraction of PMMA (the one-phase region is located above the cloud-point curve).

required temperature to generate a one-phase mixture. This limits the maximum amount of PS/PMMA in the blend with DGEBA needed to obtain a homogeneous solution at the cure temperature. Formulations including the small BDMA amount used as initiator exhibited the same cloud-point curve (one experimental point is shown as an example).

Cloud-point curves of ternary blends containing 5 and 10 wt.-% of PS + PMMA, are shown in Figure 3, represented as a function of the relative contribution of PMMA to the total thermoplastic content. Curves go through a maximum, indicating that the insolubility region (located below the curves), is increased either by replacing part of the PS by PMMA in a binary PS/DGEBA blend, or part of the PMMA by PS in a binary PMMA/DGEBA blend. In both cases, the reason for the increase in the cloud-point temperature is the lack of compatibility between PS and PMMA. Curves are asym-metric; small additions of PS to PMMA/DGEBA blends produce a steeper increase of the cloud-point temperature than in the opposite case.

BDMA-Initiated Polymerization

An initial homogeneous ternary blend was obtained by heating a PS/PMMA/DGEBA blend, containing 8.8 wt.-% total thermoplastic (PMMA/PS = 90:10) and the appropriate amount of BDMA, to 130 °C. In formulations containing the block copolymer, 0.5 wt.-% of the total thermoplastic was replaced by the same amount of PS-*b*-PMMA. Two phase-separation processes were observed for both types of formulations in the course of polymerization. A PS-rich phase was segregated at low conversions while a PMMA-rich phase was separated at more advanced conversions, in agreement with their relative solubilities in DGEBA.

In order to reduce the solubility of PMMA in the partially-polymerized epoxy, enabling its efficient phase-separation from the matrix, temperature was varied in the course of polymerization. The reaction was carried out at 130 °C until the first phase-separation process was observed. A few minutes after this point, temperature was decreased to 80 °C and kept at this value for about 5 h, when the reaction was arrested by vitrification.[7] Phase-separation of PMMA was observed during this second period.

Figure 4 shows the variation in the intensity of transmitted light as a function of polymerization time for ternary blends with or without the PS-*b*-PMMA block copolymer in the initial formulation. The insert shows a magnification to visualize the second phase-separation process.

For the sample devoid of block copolymer, a sharp decrease in the intensity of transmitted light was observed at a cloud-point time of $t_{cp} = 12$ min, due to the separation of a PS-rich phase. At $t = 15$ min, the temperature was
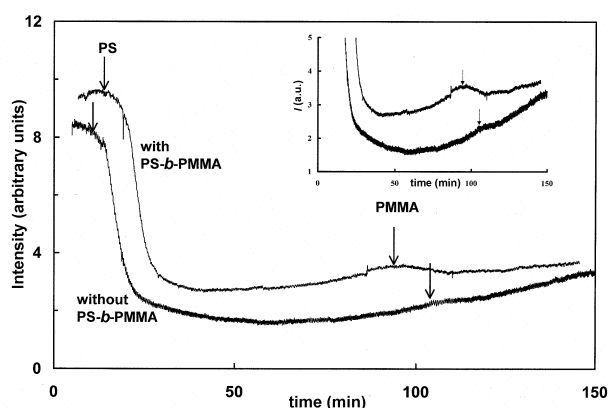
Figure 4. Intensity of transmitted light as a function of the polymerization time for formulations prepared with and without the block copolymer, cured with BDMA as initiator. The inset shows a magnification to visualize the phase separation of the PMMA-rich phase.

Figure 5. Evolution of the complex viscosity and tan δ, in the frequency range comprised between 1–100 rad · s^{-1}, during the BDMA-initiated polymerization for the formulation containing 8.8 wt.-% total thermoplastic (90 parts PMMA and 10 parts PS).

decreased to 80 °C. From about 60 min, the intensity of transmitted light began to increase due to the variation of the refractive index of the epoxy phase in the course of polymerization, approximating the value of the PS-rich phase.[7] At about 105 min, a second phase-separation process was only just evident. Plausibly, domains of the PMMA-rich phase generated at this time had small characteristic sizes, close to the detection limit of visible light.

For the sample containing the block copolymer, the separation of the PS-rich phase took place at t_{cp} = 16 min. At t = 18 min, temperature was decreased to 80 °C. The second phase-separation process was clearly observed at about 95 min, giving indirect evidence of the effectiveness of the block copolymer in increasing the characteristic size of PMMA-rich domains.

Figure 5 shows the evolution of the complex viscosity and tan δ in the course of polymerization for the formulation prepared without the block copolymer. The gel time determined from the crossover of tan δ curves at several frequencies, was t_{gel} = 115 min, slightly higher than the second cloud-point observed at t_{cp} = 105 min, with a cure cycle close to the one used in the light-transmission device. Therefore, separation of the PMMA-rich phase took place soon before gelation of the epoxy network, a fact that explains the formation of small domains that were very difficult to detect with light transmission. Similar curves were obtained for the formulation containing the block copolymer, leading to t_{gel} = 104 min; the second cloud-point time was t_{cp} = 95 min. Again, the second phase-separation process took place close to gelation.

Figure 6 a, b show, respectively, TEM micrographs of ternary blends without and with the block copolymer, at the end of the cure period at 80 °C. For the system devoid of block copolymer (Figure 6 a), the polymerization-induced phase-separation produced a diluted dispersion of PS particles with sizes in the region of 1 μm, and no
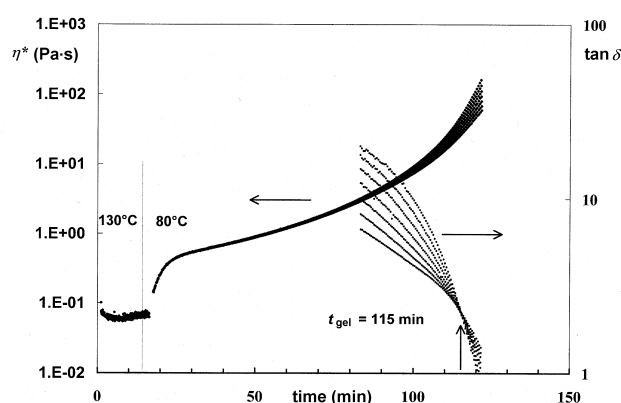
clear evidence of the presence of a dispersed PMMA phase. The characteristic size of PMMA-rich domains was outside the range detectable by TEM, due to their generation at conversions close to gelation.

The addition of 0.5 wt.-% of a block copolymer (PS-b-PMMA) to the initial formulation made the presence of a PMMA dispersed phase visible (Figure 6 b). A high concentration of small PMMA domains (100–200 nm) was observed, together with a dilute dispersion of PS particles, similar to the one generated in the absence of the block copolymer. Some of the small PMMA domains appeared to be attached to the surface of PS particles. In this case the main effect of the block copolymer was to increase the size of PMMA-rich domains segregated very close to the gel point. This is explained as follows. When PS was phase-separated, the PS blocks of PS-b-PMMA could either diffuse to the surface of PS-rich particles or phase-separate in the matrix forming a dispersion of core-shell domains (a PS-core and a PMMA-shell dissolved in the partially-polymerized epoxy). Due to the very small concentration of PS-rich particles resulting from the low amount of PS in the initial formulation, phase-separation of PS blocks in the matrix prevailed over their diffusion to PS-rich particles. At the time of PMMA phase-separation, PMMA blocks of PS-b-PMMA acted as nucleating sites for the segregation of the PMMA-rich phase. This increased the size of PMMA-rich domains, rendering them visible in TEM micrographs.

Increasing the PS concentration in the initial formulation would produce a higher initial concentration of PS-rich particles, a fact that would lead to a more efficient diffusion of PS blocks to their surface. The subsequent phase-separation of PMMA around these particles would lead to in-situ generated core-shell particles. Unfortunately, increasing the PS concentration while keeping a high PMMA amount would require very high temperatures to obtain an initial homogeneous solution (Fig-
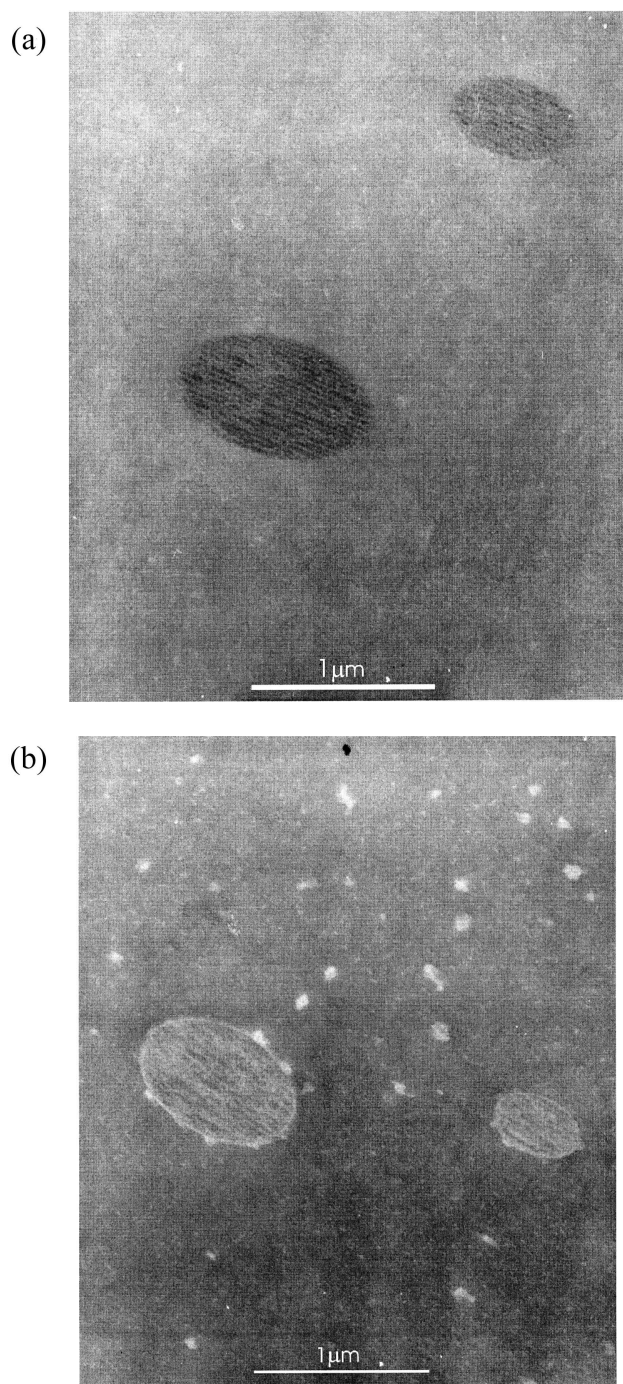
(a)

(b)

Figure 6.   TEM micrographs showing the morphologies generated in ternary blends cured with BDMA, after 5 h at 80 °C; (a) formulation containing 8.8 wt.-% total thermoplastic (90 parts PMMA and 10 parts PS); (b) formulation containing 8.3 wt.-% total thermoplastic (90 parts PMMA and 10 parts PS), and 0.5 wt.-% of PS-*b*-PMMA block copolymer.

ure 3). However, replacing BDMA by DDS as a curing agent, and using monodisperse fractions of PS and PMMA, made it possible to obtain homogeneous solutions at 135 °C with a broad range of PS/PMMA ratios.[1] Therefore, we discuss below the influence of the block
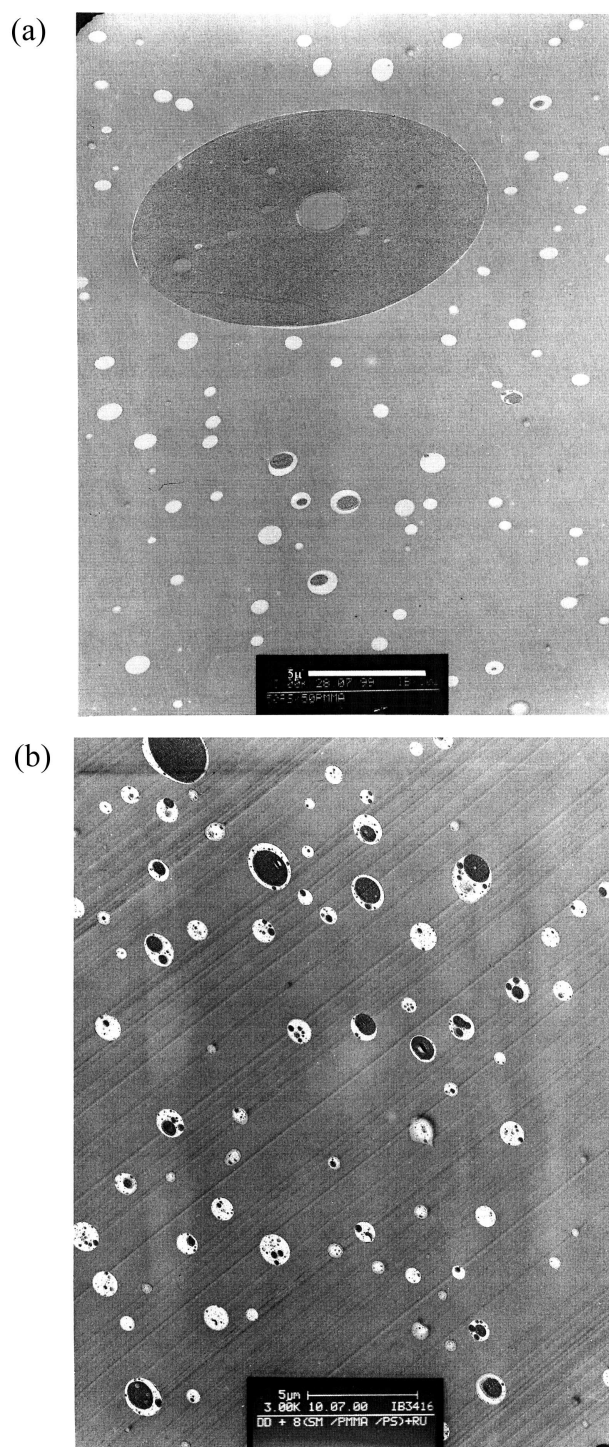
(a)

(b)

Figure 7.   TEM micrographs showing the morphologies generated in ternary blends cured with DDS, after 5 h at 135 °C; (a) formulation containing 8 wt.-% total thermoplastic (50 parts PMMA and 50 parts PS); (b) formulation containing 7.5 wt.-% total thermoplastic (50 parts PMMA and 50 parts PS), and 0.5 wt.-% of the PS-*b*-PMMA blockcopolymer.

copolymer for blends containing significant PS concentrations for ternary blends polymerized with the addition of DDS.

Stepwise Polymerization with DDS

A stoichiometric DGEBA-DDS formulation, containing 8 wt.-% total thermoplastic content (PMMA/PS = 50:50), was polymerized at 135 °C for about 5 h, when the reaction was arrested by vitrification. A double phase-separation was observed, as discussed elsewhere.[1] For comparison purposes, a sample containing 3.75 wt.-% PS, 3.75 wt.-% PMMA and 0.5 wt.-% PS-*b*-PMMA was also polymerized at 135 °C up to vitrification.

Figure 7 a, b are TEM micrographs showing, respectively, the resulting morphologies for materials with or without the PS-*b*-PMMA block copolymer. For the formulation without the block copolymer (Figure 7 a), a bimodal dispersion of PS domains (large domains with sizes in the range 5–20 µm and small domains with sizes in the range 0.2–1 µm), together with a dispersion of PMMA-rich domains with sizes in the range 0.2–1.5 µm, was observed. The relatively large characteristic size of PMMA particles arises from the fact that PMMA was phase-separated at conversions not so close to the gel conversion as in the BDMA-initiated polymerization.[1] Some of the small PS domains appeared encapsulated by a PMMA shell, a process that is driven by differences in interfacial energy between the various phases, and can be predicted by an analysis of spreading coefficients[8] and thermodynamic simulations.[9, 10] Large PS domains were presumably formed by coalescence of the small particles, due to the low viscosity of the solution at the conversion where PS was phase-separated, together with the relatively high initial concentration of PS particles.

The addition of 0.5 wt.-% of PS-*b*-PMMA to the initial formulation, produced a significant change in the morphologies generated (Figure 7 b). PMMA-rich domains of about 1 µm in size contained a dispersion of several small PS-particles. Every PS-particle appeared encapsulated in a PMMA-domain and no large PS-particles were generated. The effective diffusion of PS blocks of PS-*b*-PMMA to the surface of PS-rich particles generated at low conversions prevented their coalescence due to the shell formed by the PMMA blocks of the copolymer. At the time of PMMA phase-separation, these PMMA shells acted as nucleating sites leading to a dispersion of PMMA particles encapsulating several small PS particles.

Conclusions

A three-phase blend could be generated by a double phase-separation process induced by polymerization, starting from a homogeneous solution of PS and PMMA in a reactive epoxy solvent. PS was segregated at low conversions while PMMA was phase-separated at more advanced conversions. The addition of a small amount of a block copolymer (PS-*b*-PMMA) in formulations containing similar amounts of both thermoplastics, led to a dispersion of biphasic particles (several PS cores encapsulated by a PMMA shell), dispersed in the epoxy matrix.

The possibility of producing a stable dispersion of core-shell particles by polymerization-induced phase-separation opens a new way to modify thermosetting polymers for toughening purposes.

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