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Double Phase Separation Induced by Polymerization in Ternary Blends of Epoxies with Polystyrene and Poly(methyl methacrylate)

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ABSTRACT: Ternary blends based on a stoichiometric mixture of diglycidyl ether of bisphenol A (DGEBA) and 4,4′-diaminodiphenyl sulfone (DDS), monodisperse polystyrene (PS, 8.3×10^4 g/mol), and monodisperse poly(methyl methacrylate) (PMMA, 8.86×10^4 g/mol) were polymerized at constant temperature. Blends containing a total amount of 8 wt % of both thermoplastics (with different PS/PMMA ratios), were initially homogeneous at 135 °C. When they were polymerized at this temperature, a double phase separation was clearly observed by light transmission. At conversions close to 0.08, the system became opalescent due to the generation of a PS-rich phase; at conversions close to 0.27, a new phase separation process took place, generating a PMMA-rich phase. TEM (transmission electron microscopy) observations confirmed the existence of three different phases: the epoxy matrix, PS-rich particles with a broad size distribution, and PMMA-rich particles. Some of the PS particles appeared encapsulated by the PMMA-rich phase (core−shell particles). The double phase separation process was analyzed using a Flory−Huggins model. Experimental results could be explained by following the evolution of phase diagrams with conversion. The initial composition was located in the region of homogeneous solutions. As conversion increased, the system entered the equilibrium region between two phases (first phase separation process), and at higher conversions it attained the region where three phases coexist at equilibrium (second phase separation process). Depending on the PS/PMMA ratio, the model predicted the possibility of a phase inversion following the first phase separation process. This was also inferred from measurements of the evolution of the complex viscosity during polymerization.

Introduction

The field of thermoset−thermoplastic blends has received considerable attention during the past decade.[1] Most of these blends are prepared starting from a homogeneous solution of the thermoplastic polymer in the thermoset precursors and inducing phase separation during the thermoset polymerization.[2] A new material is generated with distinct properties with respect to those of the individual polymers.

Few studies of ternary blends involving the thermoset precursors and two linear polymers have been reported.[3−5] In two of these studies, the third component was a copolymer added to the formulation to improve adhesion between the thermoplastic domains and the epoxy matrix[3] or to decrease the average size of dispersed domains.[4] In both cases the copolymer was located at the interface, and a significant increase in the fracture toughness of the resulting materials was observed. A different aim for the use of a ternary blend was recently presented by Jansen et al.[5] Their interest was the processing of intractable polymers using reactive solvents (thermoset precursors), notably the system poly(phenylene ether) (PPE)/epoxy−amine. In blends containing significant concentrations of PPE, the advance in the conversion of the epoxy−amine reaction produced the phase separation of an epoxy-rich phase that became dispersed in the PPE-rich matrix. To control the average size of the dispersion, polystyrene (PS) was added to the initial formulation. As PS and PPE are soluble in all proportions, the continuous phase contained both components. But the presence of PS increased the viscosity of the solution at the conversion where phase separation took place, producing a decrease in the average size of dispersed domains.[5]

Systems containing two linear polymers and one thermoset may be also found in the area of interpenetrating polymer networks (IPNs), classified as semi-IPNs or pseudo-IPNs.[6,7] For example, systems containing a linear polyurethane, a linear poly(methacrylate), and a cross-linked epoxy have been described.[8] However, typical cases analyzed in the field of IPNs correspond to the simultaneous or sequential polymerization of at least two of the three components present in the initial mixture. This is not the case in the field of thermoplastic−thermoset blends where the two linear polymers are dissolved in the thermoset precursors and only one polymerization reaction takes place.

The phase behavior of ternary polymer blends is much more complicated than the case of binary blends. These systems can decompose into two or three phases. Between any two phases rich in components I and J, the third component K segregates in the interface to minimize the specific interfacial energy of the system.[9,10]

The aim of this paper is to analyze the phase separation process in a ternary blend selected in such a way that both thermoplastics exhibit a very low miscibility between themselves and also different solubilities with the thermoset precursors (but that can still be solubi-

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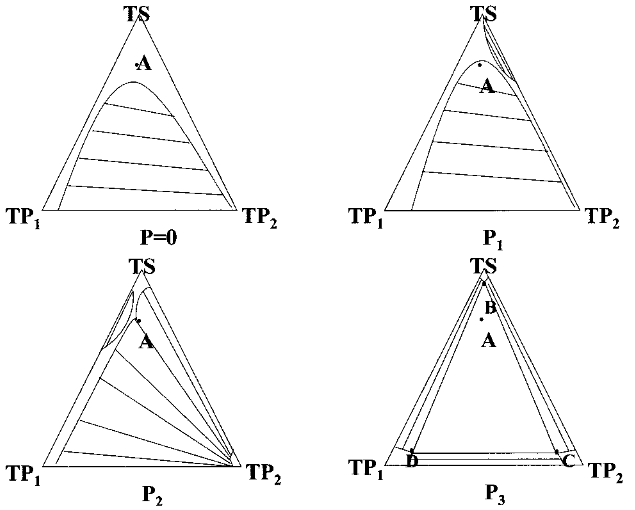

Figure 1. Phase diagrams of a ternary blend comprising one thermosetting polymer (TS) and two thermoplastic polymers (TP$_1$ and TP$_2$), at different conversions (p) of TS ($p_3 > p_2 > p_1$).

lized together in the reactive solvent). In this case, a double phase separation induced by polymerization may be expected, as qualitatively shown in Figure 1.

The initial blend of the two thermoplastics (TP$_1$ and TP$_2$) in the thermoset precursors (TS, conversion $p = 0$) lies in the homogeneous region of the phase diagram (as indicated by point A in Figure 1). As conversion increases, the system becomes less miscible, due (primarily) to the increase in the average molar volume of TS.[1,2] At $p = p_1$, the initial composition lies in the region where two phases, one richer in the binary TS−TP$_2$ and the other richer in the binary TS−TP$_1$, coexist at equilibrium. Also, a new immiscibility region between TS and TP$_2$ appears in the phase diagram. At higher conversions ($p = p_2$), the first two immiscible regions merge, and a new region of immiscibility between TS and TP$_1$ eventually appears. At this stage, the system consists of a phase rich in TS and TP$_1$ (that normally constitutes the matrix or continuous phase) and a segregated phase rich in TP$_2$. At still higher conversions ($p = p_3$), the three immiscibility regions merge, and the initial composition is located inside the region where three phases (B, C, and D) coexist at equilibrium. Now, TP$_1$ has also been segregated from the matrix, and the three resulting phases are respectively rich in each one of the initial components. This gives the possibility of generating different morphologies depending on the location of the initial composition and the phase separation mechanisms prevailing at different conversions.

For this study, the selected thermosetting polymer was a stoichiometric mixture of a diepoxide based on diglycidyl ether of bisphenol A (DGEBA) and 4,4′-diaminodiphenyl sulfone (DDS). The thermoplastics were polystyrene (PS) and poly(methyl methacrylate) (PMMA), both monodisperse. The pair PS/PMMA is “moderately” immiscible.[11] But PMMA is more miscible with DGEBA−DDS than PS.[12] So, it may be expected that PMMA (TP$_1$ in Figure 1) will be segregated from the epoxy matrix at later stages than PS (TP$_2$ in Figure 1) and that both thermoplastics will be present in distinct domains in the final morphology.

The experimental behavior of this ternary blend will be described and the observed trends analyzed using a simple thermodynamic approach based on the Flory−Huggins model. A possible phase inversion arising from model predictions is confirmed by measuring the evolution of the complex viscosity during polymerization.

Experimental Section

The thermoset precursors were a diepoxide based on diglycidyl ether of bisphenol A (DGEBA, DER 332, Dow Chemicals), with an equivalent mass of epoxy groups equal to 174.2 g, and a stoichiometric amount of 4,4′-diaminodiphenyl sulfone (DDS, Fluka). The selected thermoplastics were polystyrene (PS, Polymer Source), with $M_n = 8.86 \times 10^4$ g/mol and $M_w = 9.10 \times 10^4$ g/mol, and poly(methyl methacrylate) (PMMA, Polymer Source), with $M_n = 8.30 \times 10^4$ g/mol and $M_w = 8.60 \times 10^4$ g/mol.

Ternary blends containing 92 wt % of DGEBA−DDS and 8 wt % of PS + PMMA, with variable ratios of both thermoplastics, were prepared according to the following procedure. The mixture of thermoplastics was first dissolved in DGEBA at 140 °C, the temperature was then decreased to 135 °C, and the stoichiometric amount of DDS was added while stirring until a homogeneous solution was obtained. Binary blends containing 8 wt % of pure PS or PMMA were also prepared. At 135 °C the DGEBA−DDS reaction was relatively slow, so that the advance in conversion during the mixing step could be neglected.

Phase separation during polymerization at 135 °C, was followed using a light transmission device described elsewhere.[13]

The evolution of dynamic mechanical spectra as a function of polymerization time at 135 °C was recorded using a Rheometrics dynamic analyzer (RSA II), in a frequency range comprised between 1 and 100 rad/s. Parallel-plate geometry was used (plate diameter = 25 mm).

Transmission electron microscopy (TEM) micrographs were obtained using a JEM-200 CX device, with an accelerating voltage of 80 kV. To cut ultrathin sections at room temperature, it was necessary to advance the reaction at 135 °C well beyond the gel point. As most of the phase separation took place before gelation, only final morphologies could be observed. The presence of three phases was clearly distinguished in TEM micrographs. The distinction between PS-rich and PMMA-rich domains could be made by staining with RuO_4.[11] 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.

Results and Discussion

A. Double Phase Separation in Ternary Blends. Figure 2a,b shows experimental curves of the intensity of transmitted light as a function of polymerization time for blends prepared with ratios of PS/PMMA equal to 70:30 (a) and 30:70 (b). From $t = 0$ to $t = t_1$ intensity remains constant after some initial perturbations. At $t = t_1$ the first phase separation process ascribed to the generation of a PS-rich phase begins to take place, leading to a continuous decrease in the intensity of transmitted light. At $t = t_2$ another phase separation process assigned to the generation of a PMMA-rich phase occurs, leading to a sharp decrease in the intensity of transmitted light. The time t_1 was rather difficult to precise because of the proximity of the refractive indices of both phases and the relatively slow decrease of the intensity of transmitted light. The time t_2 was neat and was related to a change from an opalescent to an opaque (milky) state.

B. Cloud-Point Conversions. Both phase separation times were expressed as phase separation conversions using the kinetics of the DGEBA−DDS system considering the small dilution effect produced by the addition of the mixture of thermoplastics.[14]

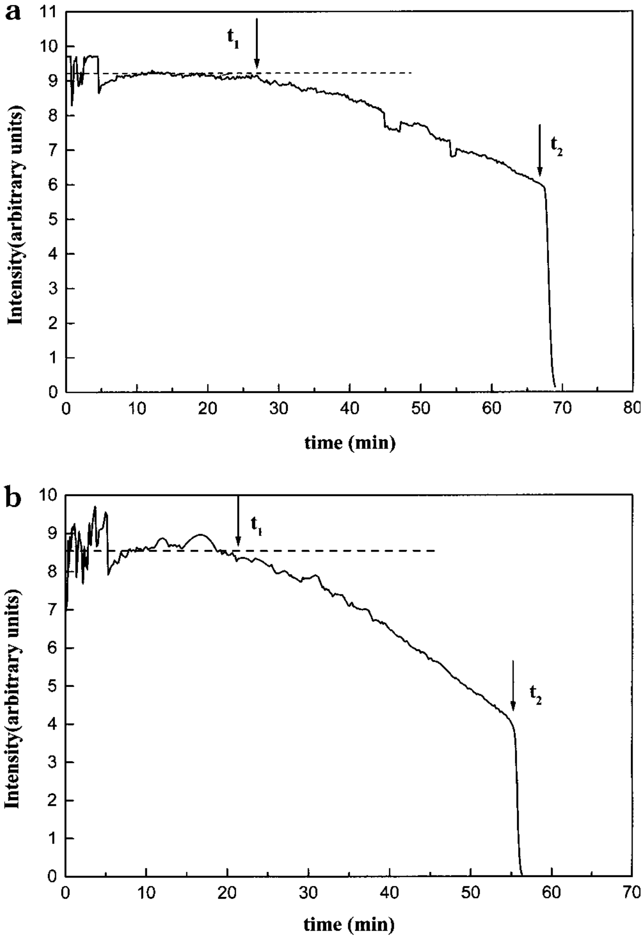

Figure 2. Intensity of the transmitted light as a function of polymerization time at 135 °C for blends prepared with a ratio PS/PMMA = 70/30 (a) and 30/70 (b). Arrows indicate the onset of both phase separation processes.

Table 1. Phase Separation Conversions (p_{ps}) in Blends Containing 8 wt % Thermoplastic, Polymerized at 135 °C

PS/PMMA	100/0	70/30	50/50	30/70	0/100
p_{ps} (1)	0.04	0.08	0.08	0.07	
p_{ps} (2)		0.28	0.27	0.22	0.32

Table 1 shows the phase separation conversions (p_{ps}) of binary and ternary blends. Results of binary blends show that PMMA is phase separated at higher conversions than PS. This reflects the higher solubility of PMMA in the epoxy matrix. Using the conversion values of binary blends, the first phase separation process in ternary blends may be assigned to the segregation of a PS-rich phase while the second process may be ascribed to the phase separation of a PMMA-rich phase.

C. TEM Micrographs. The final morphologies obtained for blends prepared with different PS/PMMA ratios are shown in Figure 3a–f. In samples stained with RuO_4, PS-rich domains appear dark while PMMA-rich domains appear bright independently of the staining process (compare 3a with 3b). In some micrographs (e.g., 3c and 3f), small dark spots present in the continuous phase are ascribed to traces of the staining process. The following features were observed for every PS/PMMA ratio:

(a) A dispersion of both types of domains is clearly identified in the micrographs. PS-rich domains exhibit a broad distribution of particle sizes. Most of the volume fraction of PS is included in very large particles (sizes in the range 5–20 μm) that are present in very small concentrations, but small PS-rich particles (sizes in the range 0.2–1 μm) are also present. Large particles appear partially detached from the matrix. The large size may be related to the low viscosity of the epoxy matrix at the time where the first phase separation process takes place.

(b) PMMA-rich domains exhibit unimodal distributions (sizes in the range 0.2–1.5 μm, increasing with the initial PMMA proportion in the blend); some of the PMMA-rich domains encapsulate small PS-rich particles (a magnified view of an encapsulated PS particle is shown in Figure 3c). In multiphase blends, encapsulation or partial encapsulation of one dispersed phase by another may take place. The process is driven by differences in interfacial energy between the various phases and can be predicted by an analysis of spreading coefficients.[15] For example, TEM micrographs of PC-encapsulated PMMA domains in a PBT matrix and PC- and SAN-encapsulated PS domains in a PBT matrix have been reported [PC = polycarbonate, PBT = poly(butylene terephthalate), SAN = poly(styrene-*co*-acrylonitrile)].[16] While in these systems encapsulation was produced during the blending process, in the present system the partial encapsulation of PS-rich particles was produced in situ during the second phase separation process.

A possible explanation of the partial encapsulation of PS particles by a PMMA-rich phase arises from the thermodynamic simulations performed by Huang et al.[9,10] for ternary polymer blends. They showed that the adsorption of a third component K in the interface between any two phases rich in I and J is a general phenomenon, and this adsorption strongly influences the microstructures during phase separation. Since the decomposition into three phases is initiated by decomposing into two phases α and β rich in A and B, respectively, and the minority component is adsorbed in the α and β interfaces during the decomposition, a third phase γ rich in the minority component will form at these interfaces.

(c) The presence of a secondary phase separation process is evident in the large PS-rich domains; small epoxy–amine-rich subinclusions appear dispersed in the large particles. They may be the result of the purification of the PS-rich phase produced by the segregation of an epoxy–amine phase as conversion increased. This secondary phase separation process puts in evidence that overall equilibrium is not attained (otherwise, these subinclusions should merge with the matrix).

The presence of two primary phase separation processes involving the successive segregation of a PS-rich phase (first primary phase separation process) and a PMMA-rich phase (second primary phase separation process) was evidenced by light transmission results and TEM micrographs. A secondary phase separation process taking place inside the large PS-rich domains was also observed. We will now try to explain this complex phase separation process through a thermodynamic model describing the behavior of the reactive blend.

D. Thermodynamic Analysis. The analysis of the phase separation process in a reactive system is usually performed taking conversion (p) as an independent variable.[17,18] For a given conversion, the present mixture contains two monodisperse thermoplastics (PS and PMMA) and a polydisperse component (the thermoset). In binary TP/TS blends it is possible to solve the

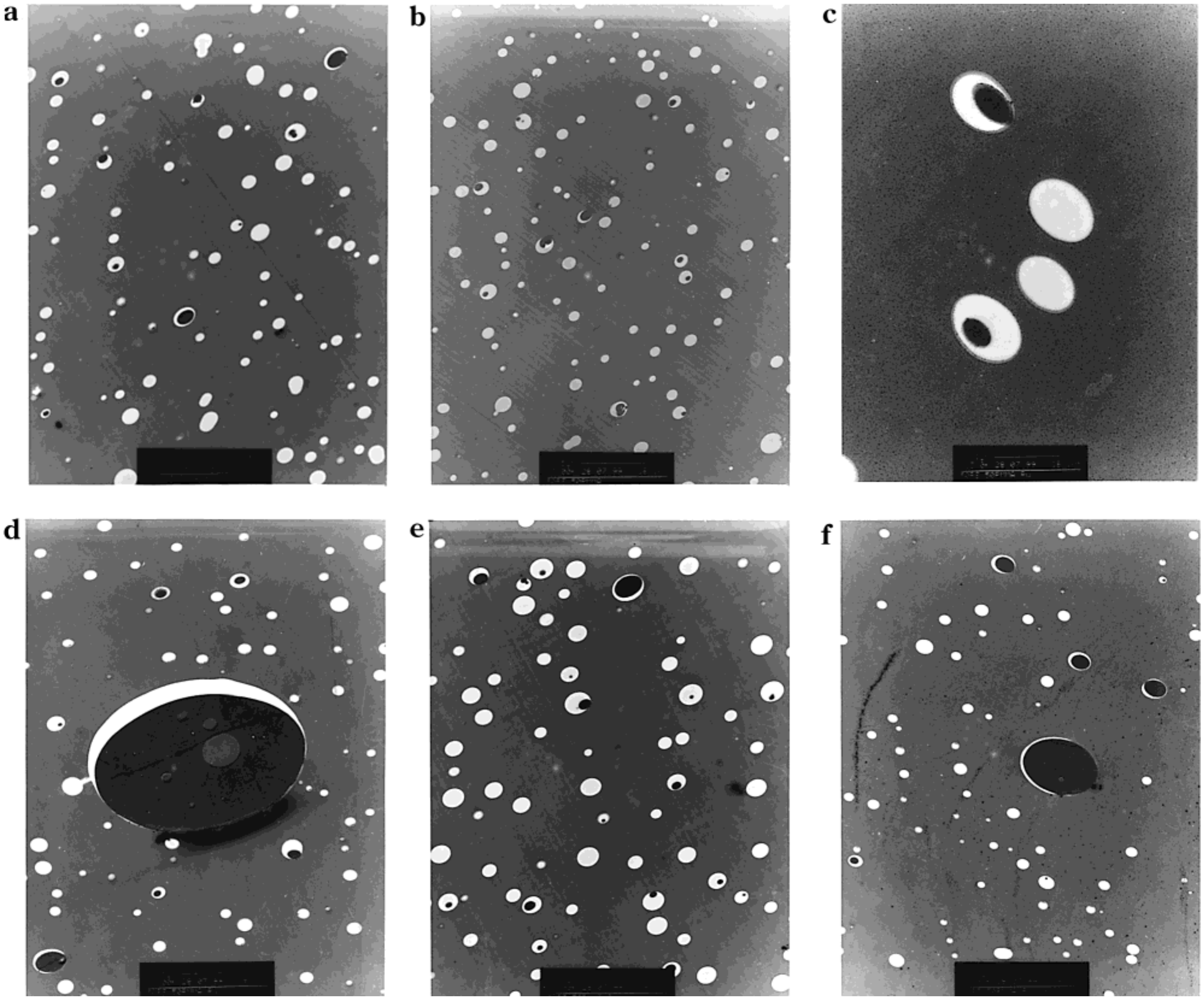

Figure 3. Transmission electron micrographs of ternary blends containing 8 wt % of PS + PMMA, polymerized at 135 °C to conversions higher than the gel conversion. Micrographs (a)−(d) correspond to blends prepared with a ratio PS/PMMA = 50/50, (e) shows a blend with a ratio PS/PMMA = 30/70, and (f) represents a blend with a ratio PS/PMMA = 70/30. All samples were stained with RuO_4 except (b), which corresponds to an unstained sample, for comparison purposes. All micrographs were taken with the same magnification (×3000) except (c), which was obtained with a higher magnification (×13 000).

thermodynamic equations taking into account the polydispersity of the thermosetting polymer in both pregel[19−22] and postgel stages.[21,22] However, in ternary blends the numerical solution becomes extremely complex if the polydispersity of the thermosetting polymer is taken into account. So, we proceed as follows: (a) we limit the thermodynamic analysis to the pregel stage where most part of the phase separation process takes place (the gel conversion for the DGEBA−DDS system is close to $p_{gel} = 0.60$); (b) for every conversion value in the pregel stage, the molar mass of the thermoset is defined as a unique value, arbitrarily taken as the number-average molar mass at the particular conversion level.

The increase in the number-average molar mass for the ideal polyaddition of a stoichiometric diepoxide−diamine mixture is given by[18]

$$M_n/M_{n,0} = 1/(1 - 4p/3) \tag{1}$$

where $M_{n,0} = 314.7$ g/mol (number-average molar mass of the initial stoichiometric mixture).

Then, for any conversion $p < p_{gel}$, the mixture of three monodisperse components will be considered: thermoset (**0**), PMMA (**1**), and PS (**2**). Using the following values for the mass densities, $d_0 = 1.22$ g/cm^3, $d_1 = 1.19$ g/cm^3, $d_2 = 1.05$ g/cm^3, the molar volumes of the constitutive units of the three polymers are given by $V_0 = 258.3$ cm^3/mol, $V_1 = 84.0$ cm^3/mol, and $V_2 = 99.0$ cm^3/mol. The smallest of these three values is taken as the arbitrary reference volume in the Flory−Huggins model, $V_r = V_1$.

The degree of polymerization of the three polymers, defined in terms of the reference volume, V_r, is given by $R_0 = 3.074/(1 - 4p/3)$, $R_1 = 886$, and $R_2 = 940.7$, where $R_i = V_i/V_r$.

In the initial system, at 135 °C, two of the possible binary systems—01 and 02—are miscible while the remaining binary (12) shows (a very low) partial miscibility. So, at $p = 0$ there will be a single immiscibility region where two phases, α and β, coexist at equilibrium. As conversion increases, partial miscibility is generated first in the binary 02 and then in the binary 01. In a ternary system where the three different binary combinations exhibit partial miscibility, there may be three different composition regions where two phases, α and β, coexist at equilibrium. We can follow the evolution of the phase diagram with conversion using the Flory−Huggins model. The following equations, derived from this model, enable one to calculate the pair of equilibrium compositions in any one of the three possible regions of immiscibility:

$$(1/R_0)\ln(\phi_{0\beta}/\phi_{0\alpha}) = (\phi_{0\beta} - \phi_{0\alpha})/R_0 + [(1 - \phi_{1\beta}) - (1 - \phi_{1\alpha})]/R_1 + (\phi_{2\beta} - \phi_{2\alpha})/R_2 + \chi_{01}\,[(1 - \phi_{1\alpha})(1 - \phi_{0\alpha}) - (1 - \phi_{1\beta})(1 - \phi_{0\beta})] + \chi_{02}[\phi_{2\alpha}(1 - \phi_{0\alpha}) - \phi_{2\beta}(1 - \phi_{0\beta})] + \chi_{12}[(1 - \phi_{1\beta})\phi_{2\beta} - (1 - \phi_{1\alpha})\phi_{2\alpha}] \quad (2)$$

$$(1/R_1)\ln[(1 - \phi_{1\beta})/(1 - \phi_{1\alpha})] = (\phi_{0\beta} - \phi_{0\alpha})/R_0 + [(1 - \phi_{1\beta}) - (1 - \phi_{1\alpha})]/R_1 + (\phi_{2\beta} - \phi_{2\alpha})/R_2 + \chi_{01}[(1 - \phi_{1\alpha})\phi_{0\alpha} - (1 - \phi_{1\beta})\phi_{0\beta}] + \chi_{02}[\phi_{0\beta}\phi_{2\beta} - \phi_{0\alpha}\phi_{2\alpha}] + \chi_{12}[(1 - \phi_{1\alpha})\phi_{2\alpha} - (1 - \phi_{1\beta})\phi_{2\beta}] \quad (3)$$

$$(1/R_2)\ln(\phi_{2\beta}/\phi_{2\alpha}) = (\phi_{0\beta} - \phi_{0\alpha})/R_0 + [(1 - \phi_{1\beta}) - (1 - \phi_{1\alpha})]/R_1 + (\phi_{2\beta} - \phi_{2\alpha})/R_2 + \chi_{01}[\phi_{0\beta}(1 - \phi_{1\beta}) - \phi_{0\alpha}(1 - \phi_{1\alpha})] + \chi_{02}[\phi_{0\alpha}(1 - \phi_{2\alpha}) - \phi_{0\beta}(1 - \phi_{2\beta})] + \chi_{12}[(1 - \phi_{1\alpha})(1 - \phi_{2\alpha}) - (1 - \phi_{1\beta})(1 - \phi_{2\beta})] \quad (4)$$

where ϕ_i ($i = 0, 1, 2$) represents the volume fraction of component i in phase α ($\phi_{i\alpha}$) or β ($\phi_{i\beta}$). Volume fractions are related through

$$\phi_{0\alpha} + \phi_{1\alpha} + \phi_{2\alpha} = 1 \quad (5)$$

$$\phi_{0\beta} + \phi_{1\beta} + \phi_{2\beta} = 1 \quad (6)$$

In the region where three phases coexist at equilibrium, the limiting tie line of each one of the three regions of immiscibility determines the composition of the equilibrium phases (each one of these equilibrium phases belongs simultaneously to two of the immiscibility regions).

To solve the set of eqs 2−6, it is necessary to estimate the values of the three interaction parameters of the binary systems: χ_{01}, χ_{02}, and χ_{12}. The first two parameters were estimated from the phase separation conversions of the corresponding binary systems (assuming a p_{ps} close to 0.1 for the phase separation of a PS-rich phase and a p_{ps} close to 0.3 for the phase separation of a PMMA-rich phase). This gave $\chi_{01} = 0.108$ and $\chi_{02} = 0.155$. The third interaction parameter was estimated by fitting the initial phase separation conversion of the ternary system. This led to $\chi_{12} = 0.008$. The order of magnitude of χ_{12} may be estimated following Stadler et al.[11] from the solubility parameters of both polymers: $\delta_{\mathrm{PMMA}} = 9.3$ (cal/cm^3)$^{1/2}$ and $\delta_{\mathrm{PS}} = 9.1$ (cal/cm^3)$^{1/2}$. Then

$$\chi_{12} = (V_{\mathrm{r}}/RT)(\delta_{\mathrm{PMMA}} - \delta_{\mathrm{PS}})^2 = 0.004 \quad (7)$$

which is very close to the one fitted by the initial phase separation conversion (as both solubility parameters are very close one to each other, the result is very sensitive to small variations in the selected individual values).

The small value of χ_{12} indicates that the pair PS−PMMA is very compatible from the point of view of the interaction energy. Their partial miscibility is the result of the very small entropic contribution to the free energy of mixing due to the large average size of the polymer chains. And the inverse occurs for the other two binaries. Despite the relatively high values of χ_{01} and c_{02}, they are miscible due to the high entropic contribution resulting from the low average size of the thermoset precursors. But as soon as the average size increases in the polymerization reaction, both TP's are segregated (first the PS, then the PMMA).

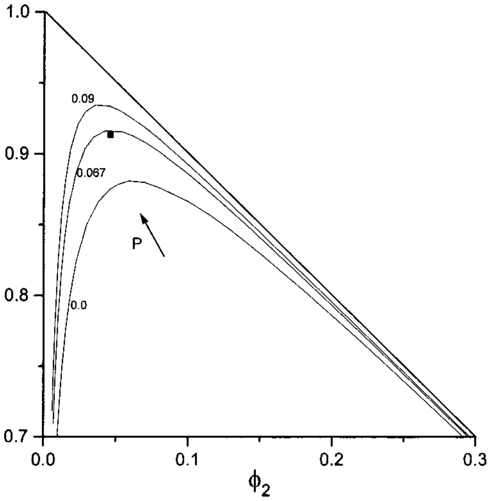

Figure 4. Phase diagram showing coexistence curves for $p = 0$, 0.067, and 0.09. The initial location of a formulation containing 8 wt % of PS + PMMA in a 50/50 weight ratio is indicated ($\phi_0 = 0.9133$, $\phi_1 = 0.0406$, $\phi_2 = 0.0461$).

The solution of the set of eqs 2−6 is not straightforward. A convenient procedure is to solve first the spinodals to fix the unstable regions of the phase diagram. Knowing this gives a hint of the location of the regions where coexistence curves must be present. This was the method we followed to calculate the different equilibria as a function of conversion.

Figure 4 shows coexistence curves for the initial system ($p = 0$) and for systems with low conversion values ($p = 0.067$ and $p = 0.09$). The location of the initial formulation containing a PS/PMMA ratio of 50/50 is indicated. Inside the coexistence curves the system is phase-separated, and outside this region homogeneous solutions are stable. So the unreacted system is a homogeneous solution. But as soon as a small conversion is achieved, the coexistence curve intercepts the initial composition and the first phase separation process may begin to take place. A very small increase in the average size of the thermoset is then responsible for the first phase separation process (generating two phases that are both rich in the thermoset, but one is enriched in PS and the other one in PMMA).

Figure 5a−c shows phase diagrams for conversions 0.12, 0.20, and 0.26. Tie lines passing through the initial formulation are also indicated. At $p = 0.26$ both phases at equilibrium are practically binary systems (PMMA/TS and PS/TS). The PS-rich phase initially contains a high fraction of dissolved thermoset. But as conversion increases, the thermoset is excluded from the PS-rich domains (note the significant increase in PS concentration when increasing conversion from $p = 0.12$ to $p = 0.26$). This explains the presence of the subinclusions observed in the large PS-rich domains.

When conversion gets close to 0.30, the second phase separation process takes place due to the partial miscibility of PMMA in the reacted thermoset. Figure 6a−d shows the evolution of regions where three phases coexist at equilibrium, for different conversion values. At $p = 0.33$, there is an equilibrium among two PMMA−TS blends with different compositions and a PS−TS blend that shows a further enrichment in PS (in fact, all these blends contain a very small amount of the third component). Outside the three-phase region there are

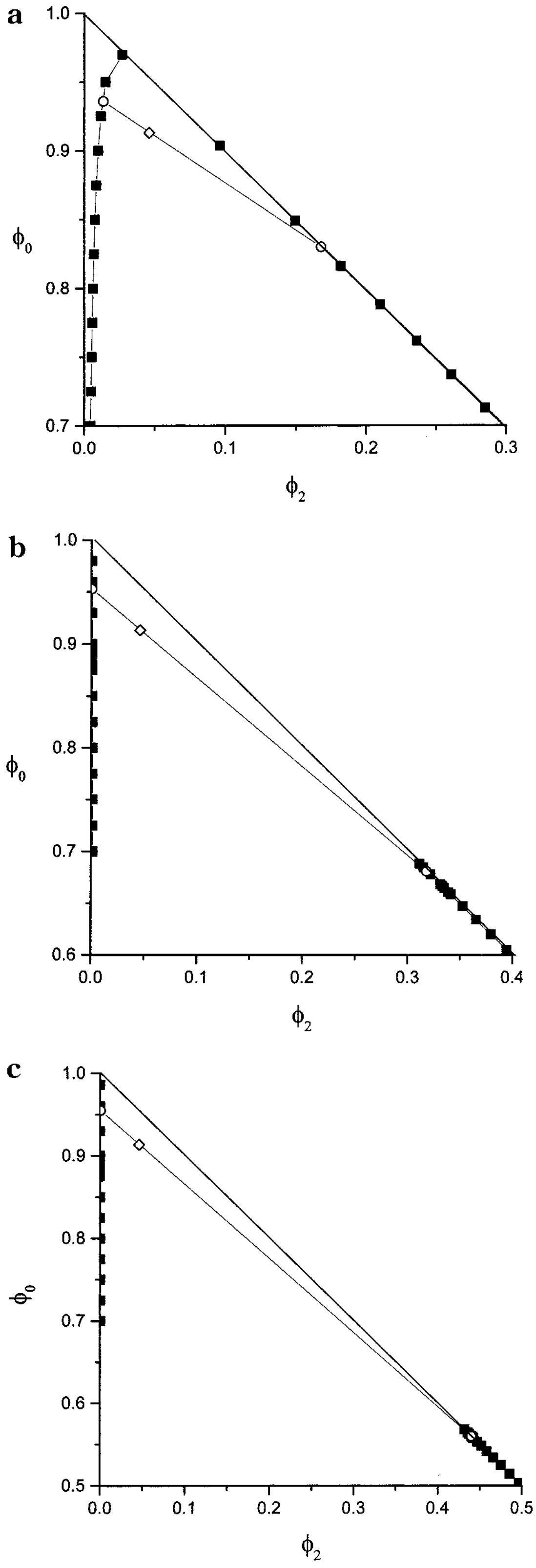

Figure 5. Phase diagrams showing coexistence curves for $p = 0.12$ (a), $p = 0.20$ (b), and $p = 0.26$ (c). The tie line passing through the initial formulation is indicated.

three other regions exhibiting binary equilibria (points represent some of the compositions of the calculated coexistence curves). As conversion increases, the three-phase region expands, producing an enrichment of each one of the phases in a pure component. At $p = 0.5$, the matrix has segregated almost all of the initial thermoplastic into two new phases that are very rich in PS and PMMA. The PMMA-rich phase dissolves more thermoset than the PS-rich phase due to the lower value of the interaction parameter with epoxy–amine species.

The simple thermodynamic model enables us to explain most of the experimental observations. The existence of two primary phase separation processes is a consequence of the evolution of the phase diagram with conversion. Secondary phase separation processes must continuously take place due to the enrichment of the segregated phases in the pure thermoplastics. The thermoset that is phase-separated in this process must, in principle, be integrated to the matrix. However, diffusional restrictions prevent this integration, particularly in the large PS-rich domains, explaining the presence of thermoset-rich subinclusions observed in TEM micrographs.

The thermodynamic model gives the ideal concentrations of different phases in an equilibrium situation. Actual compositions will evolve trying to approach the equilibrium values as a result of a competition between phase separation and polymerization rates.[2] If we further assume that the phase separation rate is larger than the polymerization rate, so that the compositions of different phases are close to the equilibrium values, the volume fraction of every phase may be calculated as a function of conversion by stating overall mass balances.

Figure 7 shows the evolution of the volume fraction of phases rich in thermoset (TS), PS, and PMMA, as a function of conversion, for blends containing different initial PS/PMMA ratios.

For PS/PMMA = 30/70 (Figure 7a), both phase separation processes are evidenced at different conversions by a decrease in the volume fraction of the thermoset-rich phase. But soon after the formation of the new phases, their volume fractions show a continuous decrease due to the enrichment process in the pure thermoplastics. At the same time, there is a corresponding increase in the volume fraction of the thermoset due to the fraction that is segregated from the thermoplastic-rich domains.

For PS/PMMA = 50/50 (Figure 7b), the situation is similar except that the volume fraction of the PS-rich phase increases with respect to the one of the PMMA-rich phase.

For PS/PMMA = 70/30 (Figure 7c), the situation changes completely. Now, the thermodynamic model predicts that it is the TS-rich phase that is initially segregated during the first phase separation process. But as conversion increases, the volume fraction of the TS-rich phase exhibits a rapid increase at the expense of the PS-rich phase. Both curves intercept, and the TS-rich phase becomes again the majority phase before the second phase separation process occurs. So, according to the thermodynamic prediction, a phase inversion must take place in formulations containing large PS/PMMA ratios.

To verify whether this phenomenon does actually occur, the evolution of the phase separation process was followed by dynamic mechanical analysis.

E. Dynamic Mechanical Analysis of the Phase Separation Process. Figure 8 shows the evolution of the complex viscosity as a function of time for blends containing different initial ratios of PS/PMMA: 30/70 and 70/30, tested at different frequencies (the lower the frequency, the higher the resulting value of the complex viscosity).

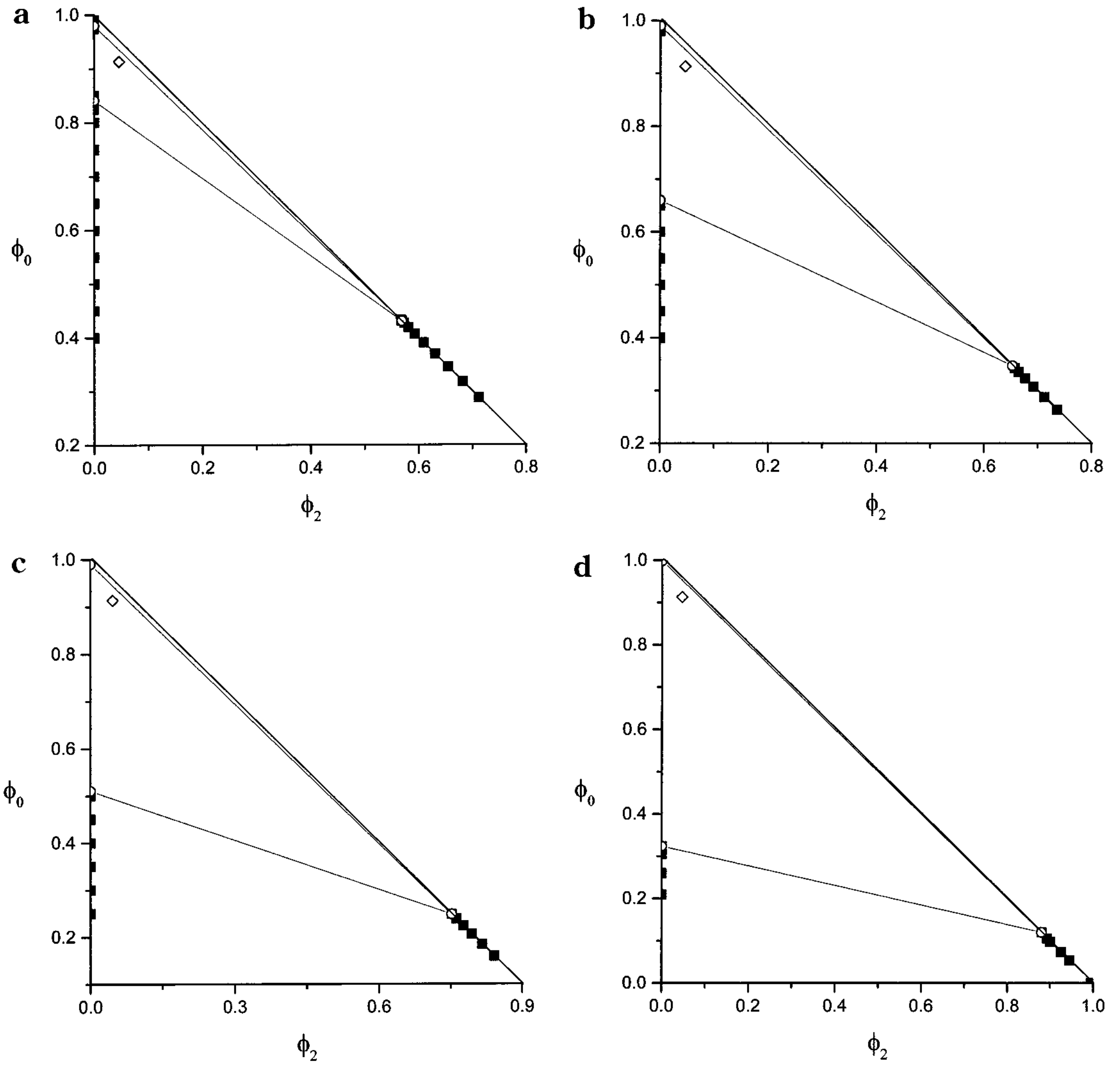

Figure 6. Phase diagrams showing a region where three phases coexist at equilibrium for $p = 0.33$ (a), $p = 0.38$ (b), $p = 0.44$ (c), and $p = 0.50$ (d).

The overall increase of the complex viscosity with time reflects the increase in the average molar mass of the thermosetting polymer in the pregel stage. Both formulations exhibit the characteristic decrease in viscosity associated with the segregation of the viscous PMMA-rich phase from the matrix, at about 5300 s (phase separation times are shifted with respect to those measured with the light transmission device, possibly due to the different temperature vs time histories). The relative decrease in the complex viscosity at this time is higher for the formulation containing the largest amount of PMMA, as expected. A significant difference is observed in the response of both systems in the low-frequency range, during the first stages of the polymerization. The blend with the lowest PS content does not provide any clear evidence of the first phase separation process. The blend with the highest PS content shows an indirect evidence of the presence of a phase-inversion process, particularly in the low-frequency range. The initial increase of the complex viscosity may be assigned to the segregation of thermoset-rich domains, leading to a high-viscous PS-rich matrix. Progressively, the rate of viscosity increase slows down, until it becomes negative (phase inversion), and finally the curve reaches the normal viscosity of the thermoset-rich phase. From this time on, the viscosity of systems with low and high PS content is almost the same, showing the PMMA segregation at about the same polymerization time.

Therefore, the dynamic mechanical analysis confirms the trends predicted by the thermodynamic model.

Conclusions

The phase separation process in a reactive ternary blend containing two thermoplastics dissolved in thermoset precursors was analyzed. Experimental observations revealed the existence of a double phase separation beginning at two different conversions. A phase richer in the least miscible thermoplastic (PS) was phase-separated at low conversions while the phase richer in the more miscible thermoplastic (PMMA) appeared at higher conversions. A partial encapsulation of PS-rich particles by a PMMA-rich phase was observed, a phenomenon that has been predicted by thermodynamic simulations of ternary polymer blends[9,10] and experimentally found in some particular blends.[15,16] The presence of thermoset-rich subinclusions inside large domains rich in PS was also evidenced. The initial PS-rich phase contains a large fraction of thermoset. As polymerization goes on, the thermosetting polymer is segregated from the PS-rich phase (secondary phase separation process). Because of the high viscosity of the PS-rich phase, the segregated TS does not merge with

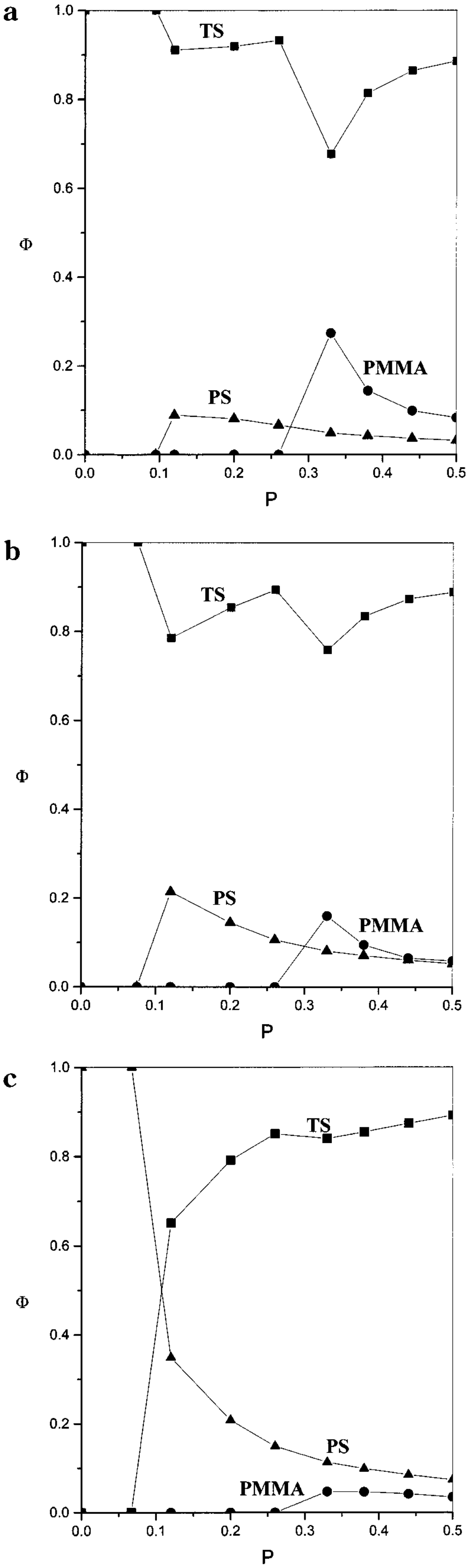

Figure 7. Volume fraction of phases rich in thermoset (TS), polystyrene (PS), and poly(methyl methacrylate) (PMMA) for initial formulations containing different PS/PMMA ratios: 30/70 (a), 50/50 (b), and 70/30 (c).

the matrix and becomes trapped as subinclusions in the PS-rich particles.

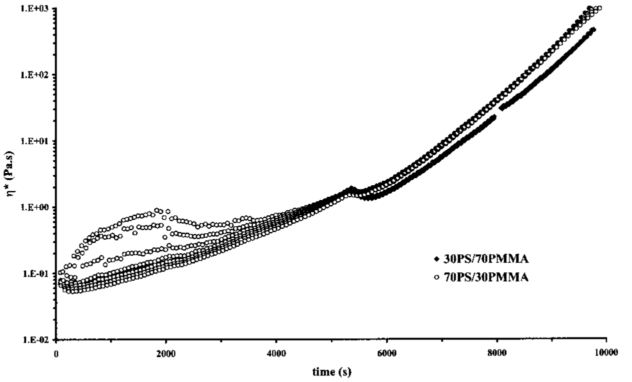

Figure 8. Evolution of the complex viscosity as a function of time for blends containing different initial ratios of PS/PMMA, 30/70 and 70/30, tested at different frequencies in the range 1−100 rad/s (the lower the frequency, the higher the resulting value of the complex viscosity).

A simple thermodynamic model describing the different equilibria as a function of conversion could explain most of the experimental findings (existence of two phase separation conversions together with the secondary phase separation processes in the segregated phases). The model also predicted the possible existence of a phase-inversion process which was corroborated by dynamic mechanical analysis.

This study opens the possibility of predicting the way to select the initial components in reactive ternary blends, or to change polymerization conditions, to obtain different morphologies and associated properties of the resulting materials. Work in this direction is in progress.

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