

Reaction-Induced Phase Separation in Epoxy/Polysulfone/Poly(ether imide) Systems. I. Phase Diagrams

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ABSTRACT: Epoxy–aromatic diamine formulations are simultaneously modified with two immiscible thermoplastics (TPs), poly(ether imide) (PEI) and polysulfone (PSF). The epoxy monomer is based on diglycidyl ether of bisphenol A and the aromatic diamines (ADs) are either 4,4'-diaminodiphenylsulfone or 4,4'-methylenebis(3-chloro 2,6-diethylaniline). The influence of the TPs on the epoxy–amine kinetics is investigated. It is found that PSF can act as a catalyst. The presence of the TP provokes an increase of the gel times. Cloud-point curves (temperature vs. composition) are shown for epoxy/PSF/PEI and epoxy/PSF/PEI/AD initial mixtures. Phase separation conversions are reported for the reactive mixtures with various TP contents and PSF/PEI proportions. On the basis of phase separation and gelation curves, conversion–composition phase diagrams at constant temperature are generated for both systems. These diagrams can be used to design particular cure cycles to generate different morphologies during the phase separation process, which is discussed in the second part of this series. © 2004 Wiley Periodicals, Inc. *J Polym Sci Part B: Polym Phys* 42: 3953–3963, 2004

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INTRODUCTION

Studies on polymeric mixtures comprising a high molecular weight thermoplastic (TP)^{1–11} and reactive thermosetting resins have significantly increased because of the development of complex morphology as the cure reaction progresses. Various types of TPs, such as poly(ether sulfone) (PES),^{1,2} poly(ether imide) (PEI),^{3,4,6} poly(ether ether ketone),³ and polysulfone (PSF),^{7–11} have

been explored to modify epoxy resins. The modifier is initially dissolved in the monomers of the system to be modified; it then phase separates because of an increase in the molecular weight of the thermosetting resin during isothermal cure. These systems represent typical examples of reaction-induced phase separation during step polymerization. Because the performance of the modified material depends on the morphologies generated and their relationships with the required properties, it is important to analyze the thermodynamic and kinetic factors involved in the phase separation process.

Another possibility for modification can be the simultaneous addition of two polymers to the

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thermosetting resin before curing. Few studies have been reported on ternary blends involving a thermoset precursor and two linear polymers.^{12–15}

The present study is intended to discuss the simultaneous modification of an epoxy matrix with two TPs. The selected TPs show different phase behavior of epoxy-TP mixtures with the temperature and are completely immiscible among them. The main objectives of the work reported here are to investigate the effect of modifiers on the thermoset chemistry using two different curing agents, to analyze the phase separation process, and to determine the corresponding phase diagrams. The use of these diagrams to produce different morphologies is reported in Part II.

EXPERIMENTAL

Materials

The chemical structures of the monomers and TPs are indicated in Figure 1. The epoxy resin

used in this work is diglycidyl ether of bisphenol A (DGEBA, MY 790, Ciba-Geigy; OH initially present = 0.06).¹⁶ Two amorphous TP polymers were used as modifiers for the epoxy resin: PSF (Udel P1700, Amoco Chemicals) with a glass-transition temperature (T_g) of 190 °C and/or PEI (Ultem 1000, General Electric) with a T_g of 227 °C. They were used as received. The reported values of the number- (M_n) and weight-average (M_w) molecular weights for PEI are 26,000 and 50,000 g mol⁻¹, respectively.²² The values for PSF are M_n = 38,000 and M_w = 63,000 g mol⁻¹.¹⁷ The epoxy resin and its blends were cured with an aromatic amine hardener, which was either 4,4'-diaminodiphenylsulfone (DDS, HT 976, Ciba-Geigy) or 4,4'-methylenebis(3-chloro 2,6-diethylaniline) (MCDEA, Lonza). The hardeners were used at an epoxy/amino-hydrogen group stoichiometric ratio of 1.

Sample Preparation

Binary blends with different compositions (PSF/PEI, PSF/MCDEA, and PEI/MCDEA from 0/100

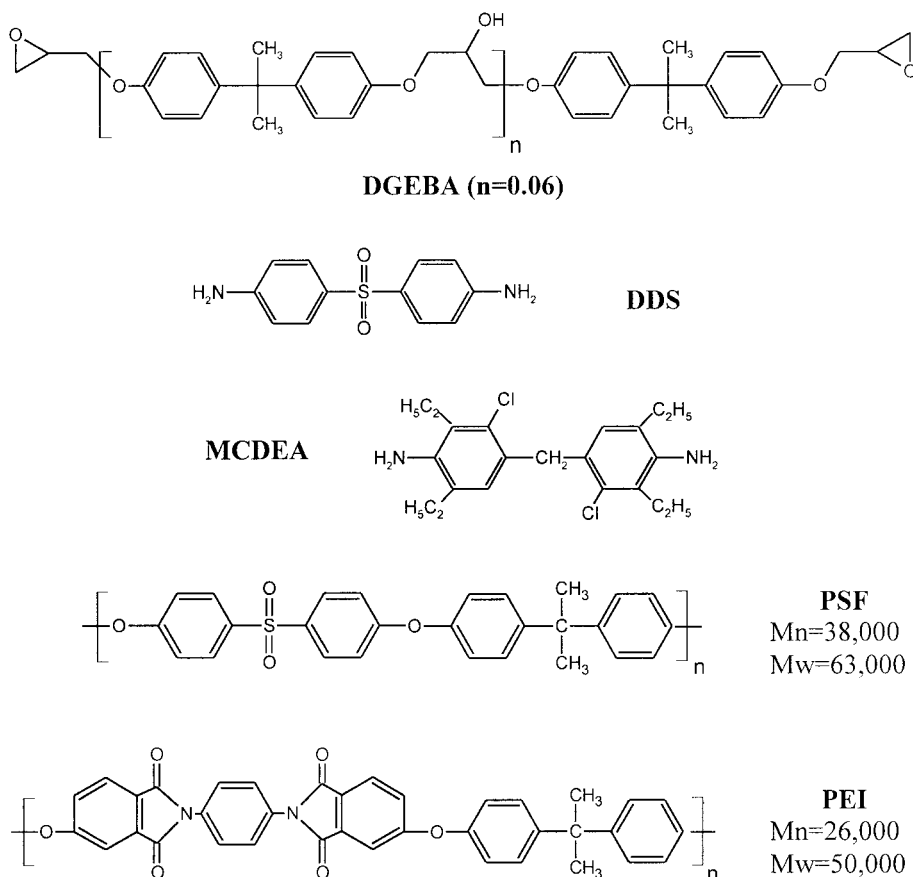


Figure 1. The chemical structures of the epoxy monomer (DGEBA), amines (DDS and MCDEA), and thermoplastics (PSF and PEI).

to 100/0) were prepared by casting at room temperature from dichloromethane (CH_2Cl_2) solutions. Thin polymer films were obtained by spreading of the solution onto different surfaces.

Modified epoxy resins containing 0–15 wt % TP were prepared using a standard procedure. We found that 15 wt % TP in the total mass represented the maximum content possible because the viscosity increased rapidly at increased loading of the TP. The TP was dissolved in CH_2Cl_2 and mixed with the resin at room temperature. Most of the solvent was evaporated at room temperature, and the residual amount was eliminated by heating at 80 °C for 24 h. In a second step, a stoichiometric amount of aromatic diamine (AD) was dissolved at 135 °C for DDS or 90 °C for MCDEA.

Measurements

Conversion versus time curves at 135 and 200 °C for pure and TP-modified epoxy–AD formulations were obtained by heating a set of tubes in an oil bath, removing one at a time at selected intervals, quenching it in ice, and determining the conversion by size exclusion chromatography (SEC).

From the analysis of the soluble products, SEC was employed to estimate the extent of reaction. A Waters chromatograph was used, which was provided with a UV detector ($\lambda = 254 \text{ nm}$) and Styragel columns (HR0.5, HR1, and HR3). The separation was carried out using tetrahydrofuran (THF) as an eluent at a flow rate of 1 mL min^{-1} . From the height of the DGEBA peak, the conversion could be obtained as¹⁸

$$x = 1 - \left(h/h_0 \right)^{1/2} \quad (1)$$

where h is the height of the peak at any conversion and h_0 is its initial value in the unreacted mixture.

The gelation time was considered to be the time at which the presence of an insoluble fraction in THF was first observed.

The cloud-point temperatures (T_{cp}) of epoxy/PEI, epoxy/PSF/PEI, and epoxy/PSF/PEI/AD unreacted mixtures, containing different PSF/PEI relations and concentrations, were determined using transmission optical microscopy (TOM). A Leica DMLB microscope provided with a video camera (Leica DC 100) and a hot stage (Linkam THMS 600) was used for this purpose. The tem-

perature was increased until a homogeneous solution was obtained, kept constant for 1 min, and then decreased at a cooling rate of 1 K min^{-1} , until the temperature at which a second phase was first observed. This procedure was repeated until a constant value was obtained.

SEC confirmed the absence of an epoxy–amine reaction during the experimental determinations of the T_{cp} . TOM was also used to determine the first phase separation times in reactive mixtures. Both phase separation and gel times were expressed as the corresponding conversion values, x_{ps} and x_{gel} , using the polymerization kinetics determined by SEC.

Differential scanning calorimetry (DSC) was performed with a Shimadzu DSC-50 under nitrogen flow to measure the heat of reaction of uncured mixtures and the T_g 's of PSF/PEI, PSF/MCDEA, PEI/MCDEA, and PSF/PEI/MCDEA blends. The heating rate used was 10 K min^{-1} in all DSC tests.

RESULTS AND DISCUSSION

Nonreactive Systems

For a satisfactory interpretation of the influence of both TP polymers in epoxy–AD mixtures, binary blends of the components were investigated first. The miscibility of the blends was judged by observation of one or two T_g 's in the DSC scans.

The DSC curves of PSF/PEI solvent-cast blends (Fig. 2) reflect a superposition of the curves of the two polymers corresponding to their content in the mixture. The glass transitions of the components are not influenced by each other because of the complete immiscibility of the blend system. Blends annealed in the DSC apparatus for 30 min at 300 °C showed two T_g 's on cooling, a fact that discounted an upper critical solution temperature (UCST) behavior for such polymer blends. This complete immiscibility can be illustrated by the morphology of the PSF/PEI blends as shown in Figure 3.

DSC measurements of blends of PSF or PEI with MCDEA revealed a single T_g positioned between the T_g 's of both components according to known mixing rules, meaning that the TPs are miscible with the AD. The Gordon–Taylor equation¹⁹ with an adjustable parametric constant for each TP fitted the T_g data of the blends. The parameter was found to be 0.28 for PSF/MCDEA and 0.40 for PEI/MCDEA blends. The behavior of

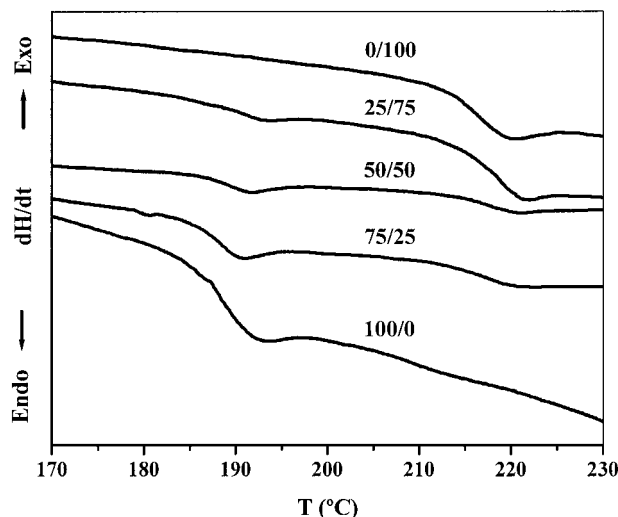


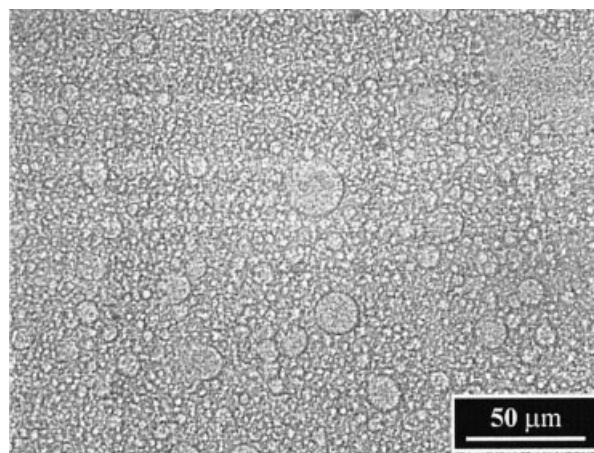
Figure 2. DSC curves of 100/0, 75/25, 50/50, 25/75, and 0/100 PSF/PEI blends that are dependent on composition.

the binary blends is also reflected in ternary blends of PSF/PEI/MCDEA. Two glass-transition temperatures were observed for all the blends that were analyzed. MCDEA distributes in the same proportion between both TPs. This was proven for different blend compositions, that is, for different contents of PSF and PEI, as well as different contents of the AD. Such behavior implies that MCDEA has no preference between both TPs. In order to confirm the above statement, FTIR studies were also made. As expected, specific physicochemical interactions between amine groups and PSF and/or PEI were not detected.

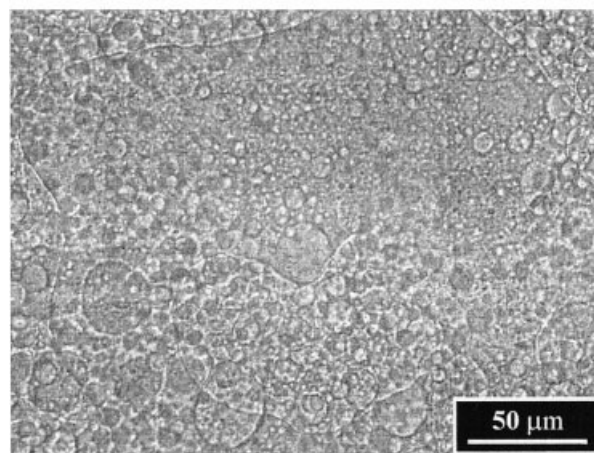
The miscibility of the blends involving DDS was not studied because it was not possible to find a common solvent for the AD and the TPs.

Studies of the phase behavior of solutions of PSF in the epoxy resin have been reported in the literature.^{20,21} The phase diagram shows demixing with lower critical solution temperature (LCST) behavior (i.e., miscibility decreases with temperature). In a previous work, we have demonstrated the miscibility of the blends by thermal analysis.¹⁶

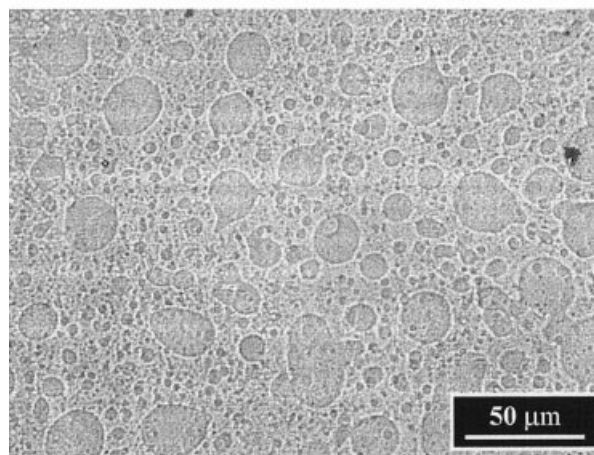
By contrast, for solutions containing PEI the corresponding phase diagram showing experimental vitrification and cloud-point curves is presented in Figure 4. As is expected in the case of UCST behavior, where miscibility increases with temperature, the cloud-point curve intersects the vitrification one. Riccardi et al.²² reported the same behavior for a similar DGEBA/PEI system.



(a)



(b)



(c)

Figure 3. Transmission optical microscopy of solution-cast binary PSF/PEI blends with ratios of (a) 75/25, (b) 50/50, and (c) 25/75.

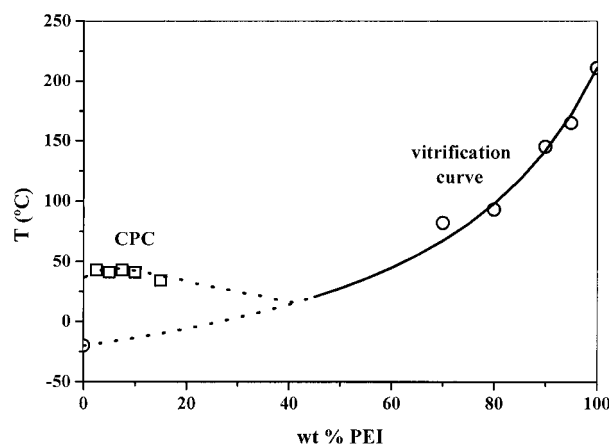


Figure 4. Cloud-point temperatures and glass-transition temperatures (T_g) versus the mass fraction of PEI in epoxy/PEI blends. The vitrification curve was estimated by the Gordon–Taylor equation using an adjustable parameter value of 0.24. CPC, cloud-point curve.

The cloud-point curves of epoxy/PSF/PEI ternary mixtures containing 5, 7, and 10 wt % PSF plus PEI are shown in Figure 5. They are represented as a function of the relative contribution of PSF to the total TP content. The system is characterized by UCST behavior, that is, the one-phase region is located above the curves. Increasing the weight percent TP leads to an increase in the temperature required to generate a one-phase mixture. The curves are not symmetric; small additions of PEI to the epoxy–PSF blends provoke

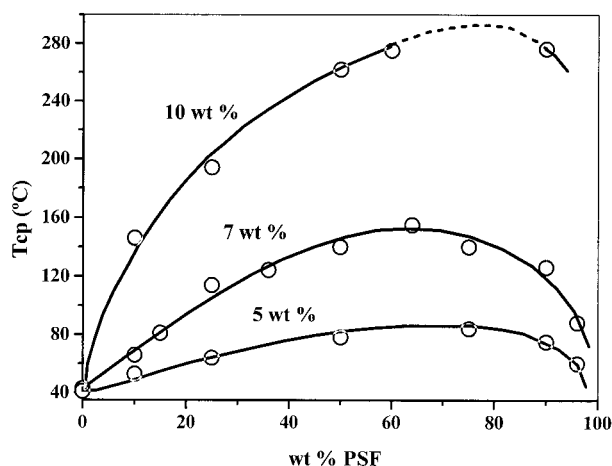


Figure 5. The cloud-point temperatures (T_{cp}) of epoxy/PSF/PEI blends, containing 5, 7, and 10 wt % total thermoplastic, as a function of the relative fraction of PSF.

a steeper increase of the cloud-point temperature than in the other case. The possibility of using high dissolution temperatures has to be discarded because of the high rate of epoxy–AD reaction under these conditions. This limits the maximum amount of PSF/PEI that can be mixed with the epoxy resin to obtain a homogeneous solution at the cure temperature (e.g., 10 wt %). Figure 6 shows the effect of the AD structure on the solubility of PSF/PEI (7 wt % total TP) in epoxy–AD solvents before any reaction has taken place. The addition of AD modifies the phase diagram. For low PSF proportion in the blends (e.g., 10%), both amines exhibit different miscibility whereas MCDEA improves the miscibility, DDS deteriorates it. The same tendency was reported by Riccardi et al.²² for a PEI-modified epoxy system. For blends containing higher proportions of PSF, both amines improve the miscibility.

Influence of TP on Epoxy–Amine Kinetics

The chemical reactions that take place during the cure of an epoxy resin are well known and have been extensively studied.^{23,24} It is generally agreed that, under appropriate kinetics conditions, the following reactions are possible in an epoxy–amine mixture: primary amine–epoxy, secondary amine–epoxy, hydroxyl–epoxy, and epoxy–epoxy. Furthermore, it is also known that compounds containing oxygen–hydrogen or nitrogen–hydrogen bonds can act as catalysts for epoxy–amine and epoxy–hydroxyl reactions. Because each of those reactions yields a new

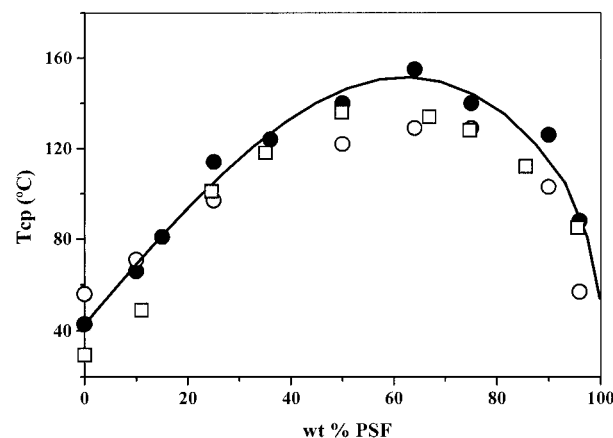


Figure 6. Cloud-point curves before reaction for blends containing 7 wt % total thermoplastic with (●) epoxy/PSF/PEI, (△) epoxy/PSF/PEI/DDS, and (□) epoxy/PSF/PEI/MCDEA.

hydroxyl group, the autocatalytic path in epoxy-amine mixtures must be taken into account. Fortunately, the general equation for the rate of epoxy-amine reactions can be simplified by a judicious choice of components and reaction conditions. First, epoxy homopolymerization is reported to occur only in the presence of a Lewis base (or acid) type catalyst²⁵ and can be neglected in its absence. Second, the importance of the etherification reaction between epoxy and hydroxyl groups has not been firmly established. It is said to depend on the temperature²⁶ and the basicity of the diamine²⁷ and increases with a large excess of epoxy groups.²⁸

The neat epoxy-AD system and its blends with 10 (PSF, PSF/PEI = 50/50) and 20 wt % PSF were cured at different isothermal temperatures, and a kinetics analysis was performed using the kinetics model reported by Girard-Reydet et al.²⁹ They studied and modeled the reaction kinetics for both neat systems (DGEBA-DDS and DGEBA-MCDEA) and also analyzed the influence of PEI on epoxy-amine kinetics.

The experimental evolution of epoxy conversion with time for modified systems is presented and compared to the neat system in Figure 7 for DDS (at 135 and 200 °C) and in Figure 8 for MCDEA (at 200 °C). The arrows indicate the phase separation times. These figures also give the kinetics model for the neat systems, consider-

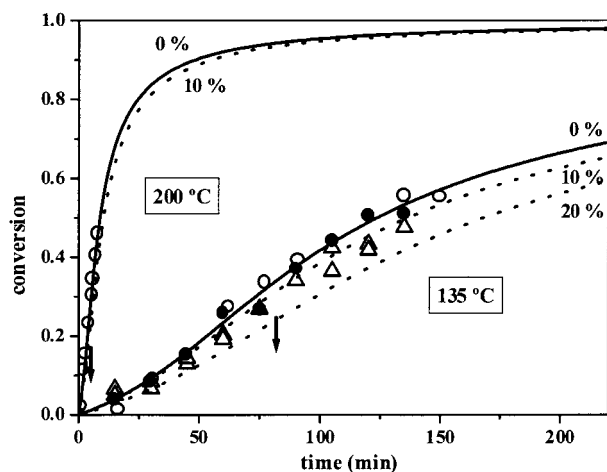


Figure 7. The epoxy conversion versus time at 135 and 200 °C for neat and modified epoxy-DDS systems: (●) neat, (○) 10 wt % PSF/PEI (50/50), and (△) 20 wt % PSF; (↓) phase separation time; (—) the initial OH in the epoxy resin; (---) the dilution effect induced by the presence of a modifier. The average error in the conversion value is ± 0.05 .

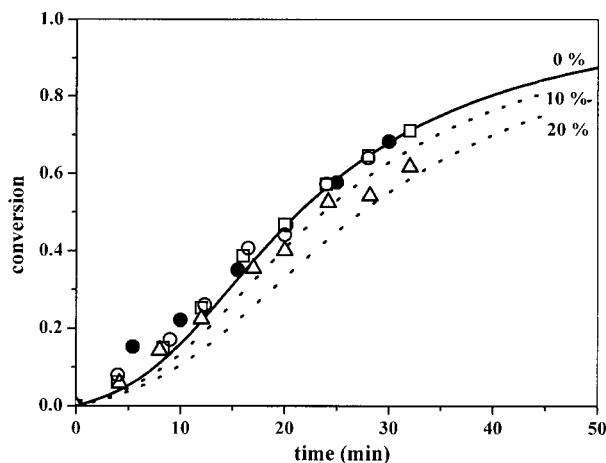


Figure 8. The epoxy conversion versus time at 200 °C for neat and modified epoxy-MCDEA systems: (●) neat, (□) 10 wt % PSF, (○) 10 wt % PSF/PEI (50/50), and (△) 20 wt % PSF; (↓) phase separation times; (—) the initial OH in the epoxy resin; (---) the dilution effect induced by the presence of a modifier. The average error in the conversion value is ± 0.05 .

ing catalytic and noncatalytic mechanisms for both ADs and taking into account the initial OH in the epoxy resin, and the kinetics prediction, taking into account the dilution effect induced by the presence of a modifier. In the case of MCDEA, etherification reactions between epoxy functions and hydroxyl groups were integrated into the kinetics model. Ritzenthaler et al.³⁰ showed that etherification reactions actually occurred in the case of MCDEA but not in the case of DDS. Because it is not believed that the size of the amine molecule affects the kinetics, the observed faster rate in DDS was attributed to its higher basicity compared to MCDEA. A similar effect was observed in an earlier study by Girard-Reydet et al.²⁹

Figures 7 and 8 show that the cure reaction rates are about the same for the epoxy and all of the blends at low levels of TP concentration (e.g., 10 wt %). No dilution effect induced by the presence of the TP was observed independently of the nature of the modifiers (PSF or PSF/PEI). The experimental results for the epoxy-DDS system modified with 10 wt % PSF/PEI (50/50) are presented in Figure 7 at two cure temperatures. The reactive solution polymerized at 200 °C, a temperature located above the T_{ep} of the initial system, phase separates during the course of polymerization. In contrast, the sample cured at 135 °C is initially immiscible (see Fig. 5). In this case, the

reaction is carried out in different phases with unknown epoxy–amine concentrations in each phase. The results shown in Figure 7 demonstrate that the overall conversion that is measured from heterogeneous blends agrees with the experimental trend for systems initially miscible for low TP concentrations.

Concerning blends with 20 wt % PSF, two different behaviors were observed according to the hardener that was used. The presence of the TP produced a slight decrease of the polymerization rate only in the case of DDS. This delay can be attributed to physical reasons as a dilution effect or viscosity increase due to the loading of a high T_g component. Furthermore, the constancy in the total heat of reaction of neat and modified systems cured with AD confirmed that PSF did not modify the mechanism of epoxy–amine polymerization. However, the experimental conversions are higher than those predicted, taking into account only a dilution effect of reactive groups for both hardeners. The theoretical curve based on a dilution effect underestimates experimental conversions. However, before phase separation, the evolution of conversions with time is nearly the same for MCDEA-cured blends. A slight decrease in the reaction rate occurs at conversions close to 0.4, an effect that may be related to the beginning of the phase separation process. In addition, whatever the curing agent, the reactions were faster in the presence of PSF. Such behavior is consistent with a PSF catalytic effect on the epoxy–amine reactions. The decrease of the reaction rate at phase separation can be explained by the effect that the presence of phenol groups at the end of their molecules¹² or any impurities in the commercial PSF produce in the reaction kinetics before phase separation. A similar phenomenon has been described using PEI as a modifier in a DGEBA–MCDEA formulation.³⁰ Other authors have reported an acceleration of the kinetics curve for TP-modified epoxies containing a relatively high fraction of modifier in the initial mixture (TP continuous phase).^{31,32}

Gelation

Table 1 shows the gel times (t_{gel}) and gel conversion results (x_{gel}) at different temperatures and modifier concentrations for epoxy–AD formulations. The lower reactivity of modified systems is also reflected in the gel time for both ADs. The modified systems exhibit a slight increase of the t_{gel} in the range of temperatures that were ana-

lyzed. On the basis of the kinetics studies, larger reaction times do not mean higher epoxy conversions in modified systems (see Figs. 7 and 8). By using the experimental evolution of epoxy conversion with time for modified systems, the t_{gel} values were transformed into corresponding conversions. As can be seen, within the experimental error of the determination of x_{gel} , the modified systems exhibit a slight increase in gel conversions only for MCDEA-cured blends. This behavior could be related to a modification of the epoxy–amine stoichiometry induced by phase separation, and it has been observed in some rubber-modified epoxy networks.³¹

Phase Separation in Reactive Mixtures

Phase separation induced by polymerization in binary blends of one TP (PSF or PEI) dissolved in an epoxy–amine reactive mixture has been reported.^{16,22} The phase behavior of ternary polymer blends is much more complicated. For systems modified with two linear polymers, the increase of the molar mass of the epoxy–amine copolymer with conversion causes the reaction-induced phase separation process of both polymers dissolved in the reactive mixture. As we discussed before, the maximum amount of PSF/PEI in the blends was limited to 10 wt %. In

Table 1. Gel Times (t_{gel}) and Gel Conversions (x_{gel}) as Function of Thermoplastic (PSF/PEI) Concentrations and Cure Temperatures for Mixtures Cured with DDS and MCDEA

Epoxy System	T (°C)	PSF/PEI (wt %)	t_{gel} (min)	x_{gel}
Epoxy-DDS	135	0	140	0.56
		20 (100/0)	165	0.56
		0	51	0.58
	160	10 (100/0)	55	
		20 (100/0)	56	
		0	12	0.58
	200	10 (50/50)	12	0.58
		10 (100/0)	13	
		20 (100/0)	14	
Epoxy-MCDEA	135	0	262	0.61
	160	0	106	0.64
		20 (100/0)	124	
	200	0	27	0.62
		10 (50/50)	30	0.68
		10 (100/0)	29	0.66
		20 (100/0)	33	0.66

blends containing this TP concentration or less, the advance in the epoxy–amine reaction produced the phase separation of a TP-rich phase dispersed in the epoxy-rich matrix. Because of the complete immiscibility of both TPs with each other, a double phase separation may be expected.

The phase behavior of binary mixtures with the temperature is different for each TP, as noted previously. Although an increase in the reaction temperature increases the miscibility in the reactive system for PEI blends (UCST), an opposite trend should have been expected for PSF blends (LCST), leading to a lower phase separation conversion. However, at the high cure temperatures needed to obtain homogeneous initial mixtures, the range of phase separation conversions of both binary systems (epoxy/PEI and epoxy/PSF) is different, depending on the AD used. For blends cured with DDS, $x_{\text{PEI}} = x_{\text{PSF}} \cong 0.30\text{--}0.35$; for those cured with MCDEA, $x_{\text{PEI}} \cong 0.45$ and $x_{\text{PSF}} \cong 0.60$. Double phase separation during polymerization (at 160 and 200 °C for DDS and 200 °C for MCDEA) was observed in ternary blends cured with both ADs using a light transmission device described elsewhere.³³ The generation of a PEI-rich phase leads to a sharp decrease of transmitted light whereas the segregation of a PSF-rich phase was difficult to determine because of the slow decrease of the intensity of the transmitted light. The latter is a consequence of the proximity of the refractive indices of both phases and explains the translucent aspect of PSF-cured blends. The assignment of the phase separation process in ternary blends was made based on the change of the intensity of transmitted light and the conversion values of binary blends. Experimental observations revealed that, in the case of DDS, both TPs phase separate at the same time, leading to a relatively gradual decrease of the intensity of the transmitted light. The similar miscibility of PSF and PEI with the thermoset precursor at high temperatures explains the fact that during the polymerization of the epoxy–DDS mixture both TPs phase separate together in PSF/PEI modified epoxy blends. Conversely, for MCDEA-cured blends the first phase separation process was assigned to the phase separation of a PEI-rich phase whereas the second process was due to the segregation of a PSF-rich phase.

From the results obtained in the kinetics section, it is possible to transform phase separation times to the corresponding conversion values using the kinetics model for the neat system. Fig-

ure 9 shows the first phase separation conversion x_{ps} versus the composition phase diagram of ternary blends containing 7 wt % total TP (PSF plus PEI) at two different curing temperatures using DDS and MCDEA as curing agents. They are represented as a function of the relative contribution of PSF to the total TP content. At these high temperatures, all the blends are initially miscible and phase separation takes place during polymerization. The experimental curves are asymmetrical for the two curing agents. In the case of DDS-cured blends, the curves show the same dependence of the miscibility on blend composition for the two temperatures under analysis. In particular, small additions of PSF produce an increase of x_{ps} in the range of PSF content between 0 and 15 wt %. After this initial increase, the x_{ps} decreases, and a rather unexpected behavior independent of the concentration over the whole range of PSF compositions is observed. Results involving MCDEA as the curing agent show that for PEI-rich solutions (Fig. 9, left) there is a concentration-independent behavior up to a PSF concentration of 10 wt %. After that there is a gradual decrease in miscibility as the PSF content is increased as a result of the concentration dependence of the cloud-point temperatures for the epoxy/PSF/PEI ternary system (see Fig. 5). As expected, in the PSF-rich solutions (Fig. 9, right) a sharp decrease of the miscibility is obtained with small additions of PEI.

For a modifier concentration of 10 wt %, the temperature required to ensure the achievement of an initial homogeneous solution is too high (see Fig. 5). The possibility of using high dissolution temperatures has to be discarded due to the fast epoxy–AD reaction, especially in the case of DDS, which is, as we pointed out, a more reactive amine. Therefore, 200 °C was chosen as the upper cure temperature that enabled us to study the evolution of phase separation in a reasonable scale of reaction times. In addition, at this cure temperature complete networks without any degradation were obtained for both AD-cured systems.

Figures 10 and 11 show the corresponding phase diagrams for blends containing 10 wt % PSF plus PEI reacted at 200 °C and cured with DDS and MCDEA, respectively. Increasing the total TP proportion provokes the appearance of an immiscibility window. In other words, the one-phase window at the beginning of the cure reaction is limited to certain blends, depending on the PSF/PEI proportions, whatever the AD employed.

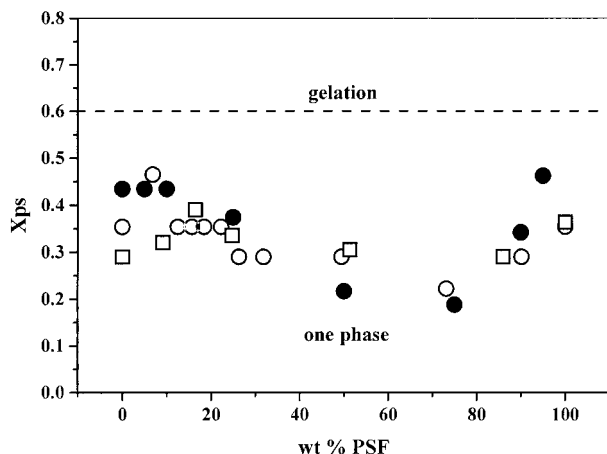


Figure 9. A phase diagram of the conversion as a function of the relative fraction of PSF for blends containing 7 wt % total thermoplastic (PSF plus PEI) cured with DDS or MCDEA at different temperatures: (□) DDS at 160 °C, (○) DDS at 200 °C, and (●) MCDEA at 200 °C. The average error in the conversion value is ± 0.05 .

However, the phase diagrams obtained for both ADs are completely different. If we first consider the results involving DDS (Figs. 9 and 10), it appears that the phase separation conversion values are nearly independent of the total TP concentration for the PEI-rich proportions. The experimental trend of the x_{ps} with the PSF/PEI ratio for 10 wt % total TP shows the same initial increase of the x_{ps} as we discussed for blends

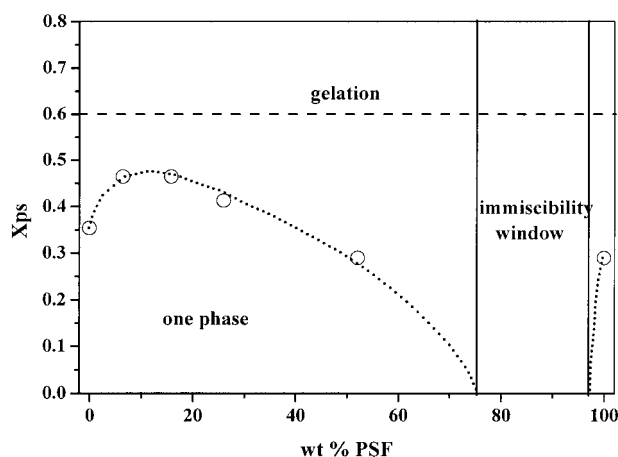


Figure 10. A phase diagram of the conversion as a function of the relative fraction of PSF for blends containing 10 wt % total thermoplastic (PSF plus PEI) cured with DDS at 200 °C. The average error in the conversion value is ± 0.05 .

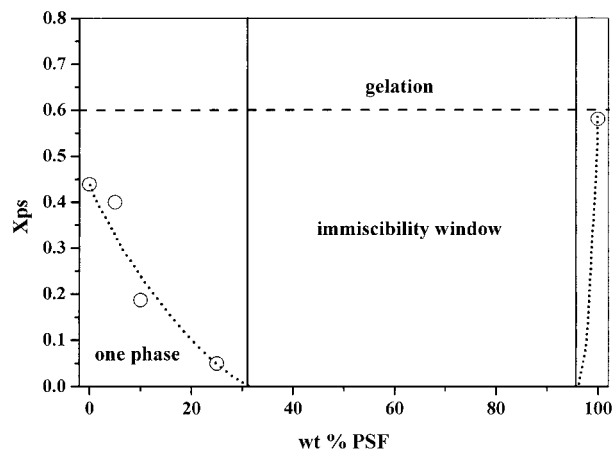


Figure 11. A phase diagram of the conversion as a function of the relative fraction of PSF for blends containing 10 wt % total thermoplastic (PSF plus PEI) cured with MCDEA at 200 °C. The average error in the conversion value is ± 0.05 .

containing 7 wt % PSF plus PEI. These experimental results are unexpected based on the cloud-point curves obtained for ternary mixtures shown in Figure 5. We should have expected that the higher the total TP content, the lower the conversion for phase separation. An important feature of the phase diagram is the location of the immiscibility window between 75 and 97 wt % PSF (Fig. 10). Contrary to the previous analysis on PEI-rich formulations, small additions of PEI to a PSF-epoxy-DDS blend produce a steeper decrease of the miscibility.

For systems cured with MCDEA, the situation is somewhat different (Fig. 11). It is worth noting the wide immiscibility window that is available. The initial heterogeneous blend compositions at 200 °C are between 30 and 97 wt % PSF. The PEI-rich formulations showed a constant decrease of x_{ps} with the addition of PSF. On the PSF-rich side of the phase diagram (Fig. 11, right), the same experimental trend as DDS-cured blends was obtained. A sharp decrease of the miscibility was observed for small additions of PEI.

Blend compositions located inside the immiscibility window (initially heterogeneous) exhibit subsequent phase separation during the polymerization of the epoxy-AD monomers. Not only the epoxy-amine species initially dissolved in the TP-rich phase but also the TP dissolved in the monomers mixture phase separate during polymerization.

When increasing the total TP content the immiscibility window became wider, meaning that

only specific PSF/PEI ratios have to be used to obtain initial homogeneous solutions at 200 °C. In formulations containing 15 wt % total TP, 10/90 PSF/PEI blends were inside the immiscibility window for both ADs.

The slight evolution of x_{gel} with composition was not considered herein, and $x_{\text{gel}} = 0.6$ was assumed throughout this study. We observed that the first phase separation takes place well before gelation for the analyzed systems.

Phase diagrams may be used to select cure cycles to obtain different morphologies. This is discussed in the Part II of this series.

CONCLUSIONS

We analyzed the reaction-induced phase separation taking place in a reactive epoxy solvent that was modified simultaneously with PSF and PEI. The epoxy/PSF/PEI blend exhibits UCST behavior at low proportions of TP. The addition of diamines was found to slightly increase the miscibility for blends with a PSF proportion higher than 10 wt %. For low PSF proportions in the mixtures, MCDEA increases the miscibility whereas DDS decreases it.

The influence of TPs on the epoxy-amine kinetics was investigated. Depending on the initial concentration of TP and AD that was used, different behaviors were observed. For a low TP concentration (10 wt %), no sudden change in the kinetic rates was detected when phase separation occurred, which was attributable to the low quantity of dispersed phase. For a higher TP concentration (20 wt %), a decrease in the reaction rate was observed when phase separation occurred for MCDEA-cured blends whereas a slight decrease of the polymerization was observed for DDS. These behaviors were explained by assuming a catalytic effect for PSF. It was found that the presence of the TP provoked an increase of the gel times.

Phase separation of two TPs from an epoxy-amine phase was analyzed in the course of reaction. Experimental observations revealed the existence of a double phase separation for blend compositions that were initially homogeneous. In contrast, phase separation was observed for blend compositions located inside the immiscibility window. Phase diagrams with different total TP contents were developed for both ADs. These diagrams can be used to select the PSF/PEI ratio in reactive blends or to change polymerization con-

ditions in order to obtain different morphologies and associated properties of the resulting materials.

With the help of these kinetics results and phase diagrams, the implications on morphologies with appropriate precuring and postcuring schedules is discussed in the second part of this series.

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