Morphology Control in Polysulfone-Modified Epoxy Resins by Demixing Behavior

M. I. Giannotti, M. S. Solsona, M. J. Galante, P. A. Oyanguren

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

ABSTRACT: Polysulfone (PSu) was used as a modifier of epoxy/aromatic diamine formulations. Two epoxy monomers, based on diglycidyl ether of bisphenol A (DGEBA), were used. The cure agent was 4,4'-diaminodiphenylsulfone. PSu was miscible with DGEBA, as shown by the existence of a single glass-transition temperature within the whole composition range. The effect of PSu addition on the cure kinetics was investigated. The reaction rate of the epoxy–amine species was slightly lower in the presence of PSu. The morphology was analyzed by optical and scanning electron microscopy. A range of microstructures were obtained by control over the cure temperature, the amount of PSu incorporated, and the molecular weights of the epoxy resins. The variations in the morphology resulted from the different stages of demixing, which were arrested because of the different developments of the viscosity of the system. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 405–412, 2003

Key words: phase separation; blends; morphology

INTRODUCTION

Blends of ductile thermoplastics with thermosetting resins are widely used as matrices for high-performance composites because of their combination of stiffness and toughness. Various types of thermoplastic, such as poly(ether sulfone),[1,2] poly(ether imide) (PEI),[3–5] polysulfone (PSu),[6–10] and poly(ether ether ketone),[11–13] have been explored for the modification of epoxy resins. In a thermoset/thermoplastic blend, starting from a homogeneous mixture, the system is thrust into a two-phase regime by an increase in the molecular weight of the epoxy at an early stage of curing. The structure is fixed by gelation or vitrification at a late stage of curing. Depending on the solution viscosity, which determines the rate of demixing and the rate of the viscosity increase, the degree of demixing and, therefore, the morphology can be varied.

As a part of a series of studies on the modification of epoxy resins in this laboratory,[14–20] this work concerns the investigation of bifunctional epoxy–PSu blends and the effects of differences in the reaction kinetics of epoxy–amine, the cure temperature, and the blend composition on the morphologies generated.

EXPERIMENTAL

Materials and preparation of the samples

Two diglycidyl ether of bisphenol A (DGEBA) epoxy resins were used in this program, Dow DER 332 and Ciba–Geigy MY 790, with number-average molecular weights of 349 and 344 g mol^{-1} and hydroxy/epoxy ratios of 0.015 and 0.007, respectively.

The selected hardener was 4,4'-diaminodiphenyl-sulfone (DDS; HT 976 Ciba–Geigy). It was used in stoichiometric proportions with respect to the epoxy monomer.

A commercial-grade PSu (Udel P1700, Amoco Chemicals) was used as a modifier.[16] The PSu concentration in the mixture (mass of PSu/total mass) was varied (0–20 wt %).

The mixtures were prepared as follows. DGEBA and the required amount of PSu were dissolved in methylene chloride. Most of the solvent was evaporated at room temperature, and the residual amount was eliminated via heating at 80°C for 24 h. The amine was added at 135°C. A clear and homogeneous solution was obtained.

Techniques

^{1}H-NMR spectra of epoxy resins were recorded on a Bruker AC200 instrument at 200 MHz.
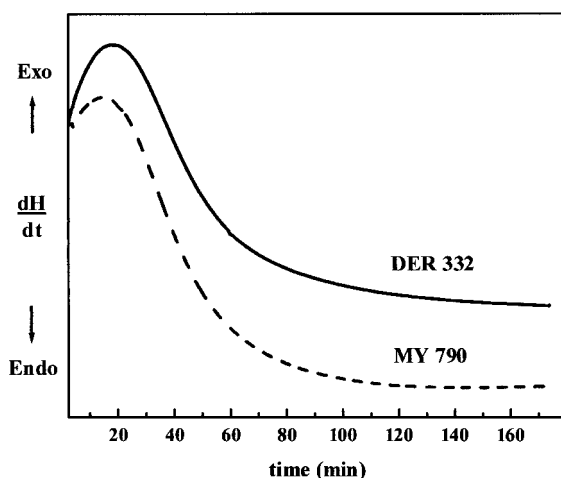
Figure 1 DSC response in the isothermal mode for DGEBA/DDS at 160°C for MY 790 and DER 332 epoxy resins.

Differential scanning calorimetry (DSC) was carried out with a Shimadzu DSC-50 apparatus (Kyoto, Japan). DSC was used to carry out the polymerization in the isothermal mode under a nitrogen atmosphere.

Conversion–time curves at 100, 120, 135, and 160°C for pure and PSu-modified epoxy–amine formulations were obtained by the heating of a set of tubes in an oil bath, their removal one at a time at selected intervals, and their quenching in ice; the conversion was determined by size exclusion chromatography (SEC).

From an analysis of the soluble products, SEC was employed to estimate the extent of reaction. A Waters chromatograph (Milford, MA) was used that was equipped with an ultraviolet detector (λ = 254 nm) and the following Styragel columns: HR0.5, HR1, and HR3. The separation was carried out with tetrahydrofuran (THF) as an eluent at a flow rate of 1 mL min^{-1}. From the height of the DGEBA peak, the conversion (x) could be obtained as follows:[21]

$$x = 1 - (h/h_0)^{1/2} \tag{1}$$

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 is considered to be the time at which the presence of an insoluble fraction in THF is first observed. Cloud-point times (t_{cp}'s) were expressed as the corresponding cloud-point conversions (x_{cp}'s), with the polymerization kinetics determined by SEC.

A Leica DMLB microscope (Wetzlar, Germany) provided with a video camera (Leica DC 100, Heerbrugg, Switzerland) and a hot stage (Linkam THMS 600) was used to determine cloud-point temperatures (nonreactive mixtures), t_{cp}'s (reactive mixtures), and final morphologies.

Fracture surfaces produced at room temperature were observed by scanning electron microscopy (SEM; JEOL JXA-8600). Before being tested, the samples were coated with a fine gold layer.

RESULTS AND DISCUSSION

Kinetic model

Isothermal DSC data obtained for DGEBA/DDS reaction at 160°C for both epoxy resins are shown in Figure 1, which illustrates the different rates of the curing process. No significant difference in the average heat of reaction between both epoxy resins was found. The lower reactivity of DER 332 is also reflected in the gel times. An inverse proportionality of the natural logarithm of the gel times on the cure temperature for both epoxy resins is displayed in Figure 2. The use of DER 332 resulted in an increase in the gel times in the range of temperatures analyzed.

The unmodified epoxy–amine curing mechanism is well known to be autocatalytic in nature;[22,23] that is, the hydroxy groups produced during cure, as well as those initially present, catalyze the curing reaction itself, particularly at low conversions before vitrification. The prediction based on the structures reported by epoxy resin suppliers contradicts the experimental results. MY 790 reacts faster than DER 332, even though the former has a lower content of hydroxy groups initially present. To understand this behavior, we analyzed the chemical structures of both commercial products. Some alternative analytical methods, such as ^{1}H-NMR and SEC, were employed. In ^{1}H-NMR investigations, the region of interest extends from 2.6 to 3.0 ppm, in which the absorption of OH is expected to be located. The integrals of the absorption
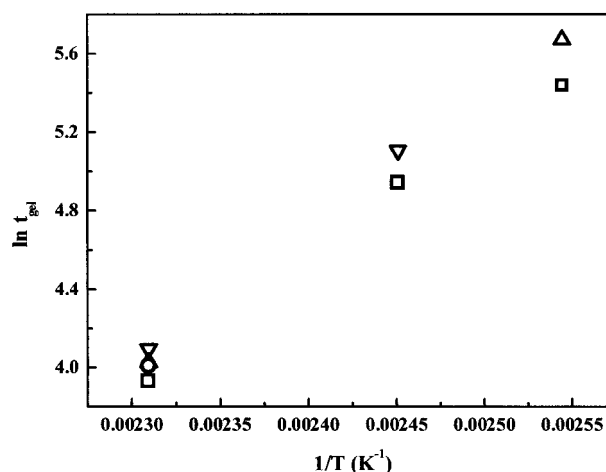

Figure 2 Natural logarithm of the gel time versus the reciprocal temperature for epoxy resins cured with DDS and containing different proportions of PSu: ($\square$) MY 790/DDS, ($\triangledown$) DER 332/DDS, ($\bigcirc$) MY 790/DDS with 10 wt % PSu, and ($\triangle$) MY 790/DDS with 20 wt % PSu.

Figure 3 SEC chromatograms of MY 790 and DER 332.

Figure 5 Relationship between the value of T_g (from DSC) and the composition in mixtures of PSu with MY 790 epoxy resin monomer: (–) eq. (1) with $k = 0.26$.

peaks for MY 790 correspond to a fraction of protons approximately 2 times larger than those for DER 332. Figure 3 shows size exclusion chromatograms of both epoxy resins. The peak corresponding to high molecular weight species is approximately 1.5 times higher for MY 790. These experimental results, in addition to the weight per epoxy equivalent reported in the literature, 176 g equiv^{-1} for MY 790[24,25] and 174 g equiv^{-1} for DER 332,[26] indicate that the polydispersity index of MY 790 is considerably higher than the value reported by the supplier.

Figure 4 shows conversion–time curves obtained at different temperatures for the neat system and for a formulation containing 20 wt % PSu at 135°C. In the
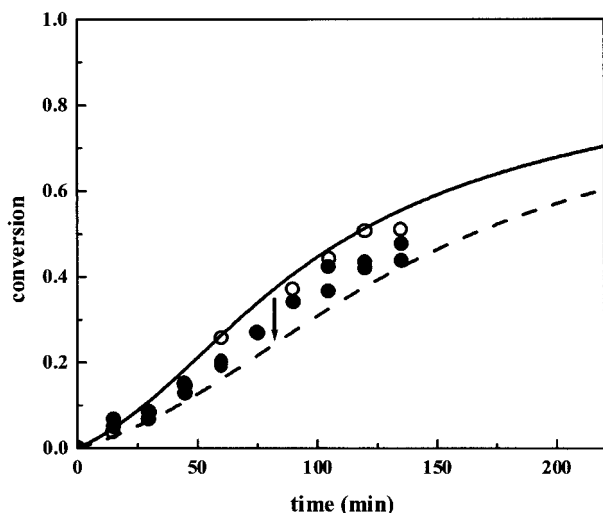

Figure 4 Conversion–time curves for (○) the neat MY 790/DDS system and (●) the system containing 20 wt % PSu: (—) kinetic prediction for the neat system and (–) kinetic prediction for the 20 wt % PSu-modified system. The arrow indicates t_{cp}.
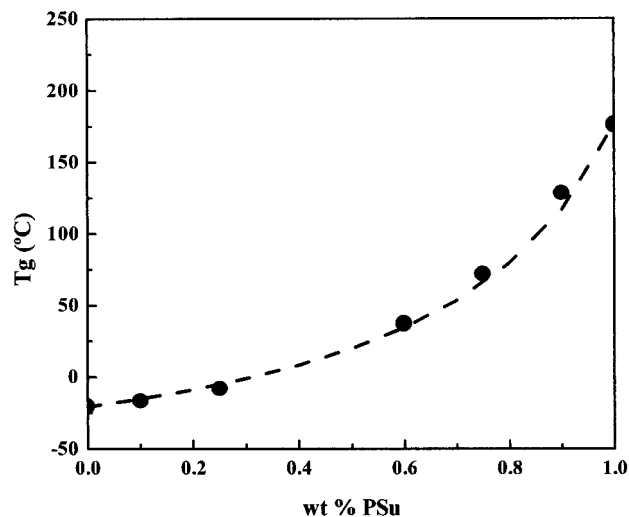
same figure, the kinetic modeling of the neat system, described by Girard-Reydet et al.,[26] and the kinetic prediction considering a dilution effect induced by the presence of the thermoplastic, described by Bonnet et al.,[27] are given. For the neat system, the best fit was obtained for a concentration of OH initially present in the MY 790 epoxy resin equal to 0.06. A comparison of the experimental evolution of the epoxy conversion and the prediction of the kinetic model (see the dashed line in Fig. 4) at 135°C shows no dilution effect for the PSu-modified system. Similar results were previously reported.[16] The experimental epoxy conversion, which is measured after phase separation, is an overall measurement of conversion in both phases. The presence of PSu led to retardation of the epoxy–amine cure kinetics, particularly after phase separation (t_{cp} indicated by an arrow). This behavior is probably due to the high viscosity of the homogeneous solution before the formation of a highly viscous PSu-rich phase during demixing. The influence of PSu on the kinetics was confirmed by the increase in the gel time at all temperatures (Fig. 2).

Binary DGEBA/PSu blends

At room temperature, blends of PSu with DGEBA resin are transparent over the whole composition range; this indicates complete miscibility. This conclusion is confirmed by thermal analysis studies, which show a single glass-transition temperature (T_g) that increases with the PSu concentration, as shown in Figure 5. The data fit the Gordon–Taylor equation:[28]

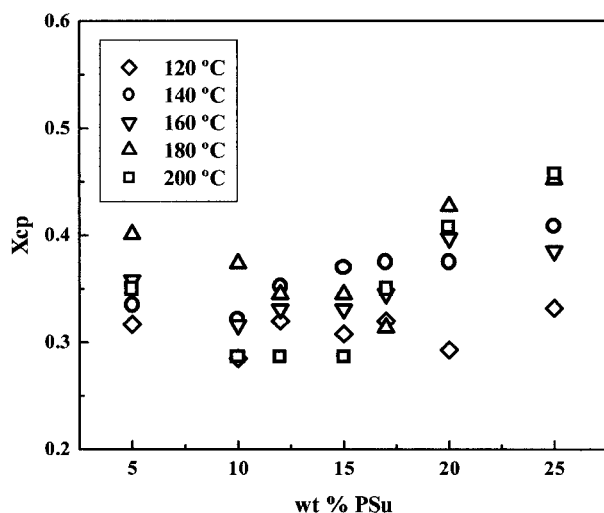$$Tg = (w_1 T_{g_1} + k w_2 T_{g_2})/(w_1 + k w_2) \qquad (2)$$

Figure 6 Conversion–composition diagram obtained at different cure temperatures for the PSu/MY 790/DDS system showing experimental cloud-point data at the start of phase separation (x_{cp}).

where the adjustable parameter k is 0.26. This result suggests a weak interaction between DGEBA and PSu.

Phase separation of PSu in reactive mixtures

Figure 6 shows a conversion–composition diagram for 120–200°C. As we discussed in the previous section, the reactivity of PSu-modified epoxy–amine mixtures is slower than that of the neat system but much faster than the predicted dilution effect. For example, for an initial 20 wt % PSu blend cured at 135°C, the cloud point is attained at 82 min, and the corresponding value of x_{cp} is 0.3. At this reaction time, the conversion predicted by the kinetic model for the neat system is $x = 0.32$, whereas for the dilution effect, x is 0.17. From these results, it is now possible to transform t_{cp}'s into conversions with the kinetic model for the neat system. This assumption introduced an error of less than 10% in the predicted x_{cp} value for a high content of the thermoplastic.

Binary mixtures of DGEBA and PSu exhibit lower critical solution temperature (LCST) phase behavior.[29] Therefore, an increase in the miscibility with a decreasing cure temperature in the reactive system should have been expected. However, the influence of the cure temperature is masked within the experimental error of the determination. It is, therefore, difficult to clearly understand the LCST behavior of PSu.

Phase morphology

The microstructural analysis of PSu-modified mixtures was conducted by optical microscopy (OM) and SEM.

Morphologies are controlled by many factors, such as the miscibility, modifier concentration, temperature, and reaction rate. The most important factor controlling the morphologies generated is the location of the composition of the initial blends, with respect to the critical composition. For blends located at the left of the critical point, the dispersed phase consists of a random distribution of spheres rich in PSu. The resulting morphologies of mixtures containing 5 and 10 wt % PSu cured at 200°C are shown in Figure 7. As can be seen, at low loadings, spherical particles of a PSu-rich phase ranging in size from 1 μm in diameter for 5 wt % PSu [Fig. 7(a)] to 1.5 μm in diameter for 10 wt % PSu [Fig. 7(b,c)] were dispersed in a continuous epoxy-rich phase. The epoxy resin that was employed played a minor role in the morphology developed, as observed in Figure 7(b,c).

For compositions located close to the critical point, spinodal demixing is expected to occur, and bicontinuous structures may be obtained. When the system is changed by an increase in the amount of PSu incorporated to a 15 wt % loading, a dramatic morphological change takes place, and the final morphology is strongly affected by minor changes in the sample composition and cure temperature. Plaques with both epoxy resins were prepared under the same experimental conditions, fractured at room temperature, and observed by OM. The resulting micrographs are presented in Figure 8. The dark region is ascribed to the PSu-rich phase, whereas the bright region corresponds to the epoxy-rich phase. For the DER 332 epoxy resin, a complex morphology, consisting of large domains rich in PSu, exhibiting irregular shapes, and dispersed in a continuous epoxy matrix, was found [Fig. 8(a)]. However, for the MY 790 epoxy resin, a phase-inverted morphology was observed in which particles rich in epoxy–amine (12 μm in diameter) were dispersed in a continuous matrix rich in PSu [Fig. 8(b)]. It is worthwhile to note that small epoxy inclusions appeared within the PSu-rich phase. The coexistence of a continuous phase and a disperse phase was not the result of different mechanisms of phase separation in the sample, but of the breaking and coarsening of an initially continuous PSu-rich phase. The difference in the reaction kinetics is a factor that must be taken into account. The epoxy resin selected will determine the rate of reaction at any given temperature and, therefore, the period during which phase separation can take place. These two competing processes, the phase separation and the cure reaction, are controlling factors that determine the final morphology in the reaction-induced phase-separation process. It seems that 15 wt % PSu is in the transition loading range, in which small changes in the experimental conditions provoke a different morphology. The initial miscibility also influences the resulting morphologies. Unfortunately, we could not determine
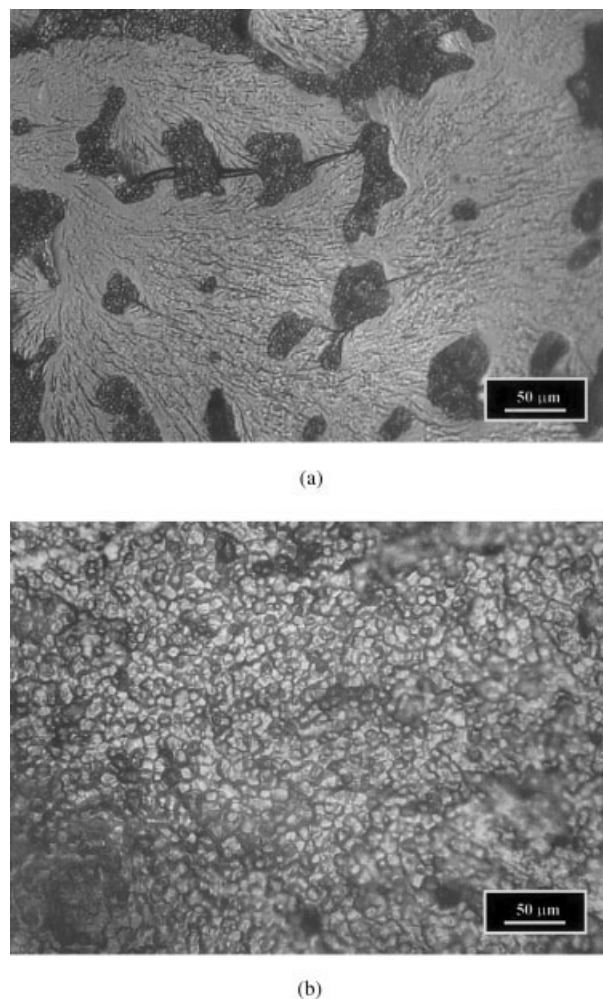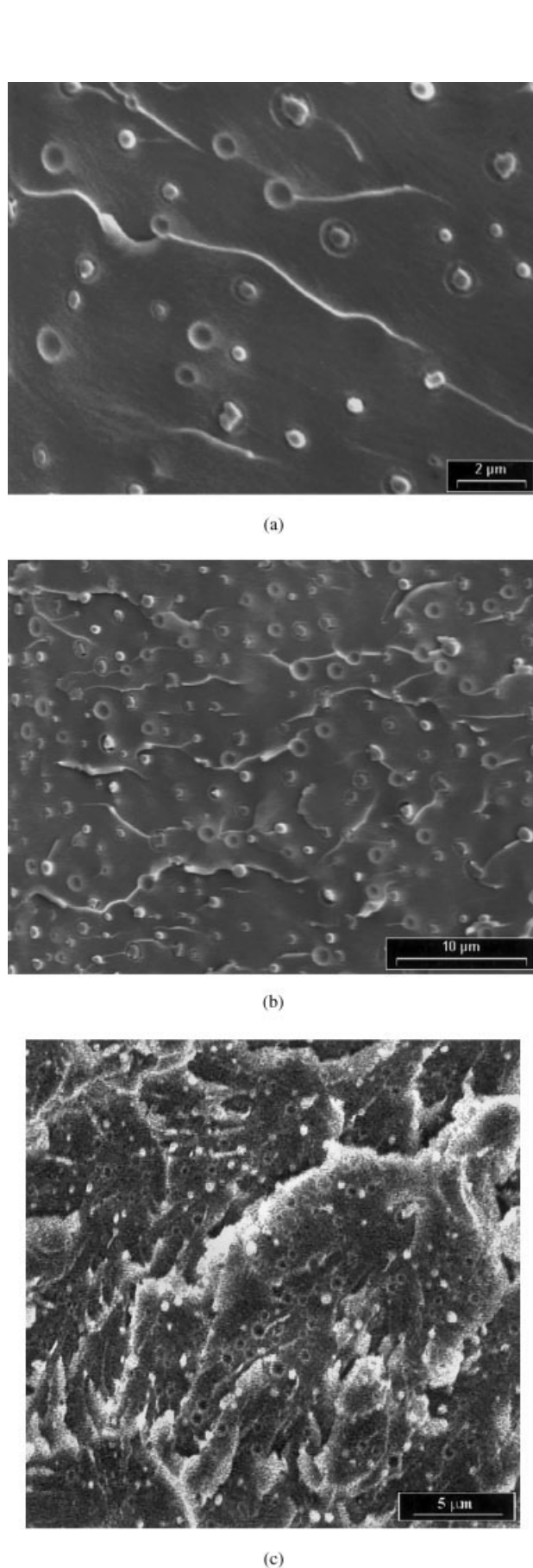
(a)

(b)

(c)

(a)

(b)

Figure 8 OM micrographs of fracture surfaces of plaques containing 15 wt % PSu that were prepared with different epoxy resins cured simultaneously at 200°C: (a) DER 332 epoxy resin and (b) MY 790 epoxy resin.

experimentally the cloud-point curve (CPC) for DGEBA/PSu because of the high temperatures at which the system phase-separates. However, we have determined the CPCs for mixtures of PEI (Ultem 1000, General Electric (Pittsfield, MA); number-average molecular weight = 12,000, weight-average molecular weight = 30,000 g mol^{-1}) and DGEBA. Both epoxy monomers of different molar masses exhibited the same miscibility behavior with PEI. Considering the previous discussion and assuming that the increase in the molar mass of DGEBA from 349 (n = 0.03, DER 332) to 357 g mol^{-1} (n = 0.06, MY 790) does not produce a noticeable shift in the location of the misci-

Figure 7 SEM micrographs of samples cured at 200°C and postcured at 230°C containing different amounts of PSu and prepared with different epoxy resins: (a) 5 wt % PSu and MY 790 epoxy resin, (b) 10 wt % PSu and MY 790 epoxy resin, and (c) 10 wt % PSu and DER 332 epoxy resin.
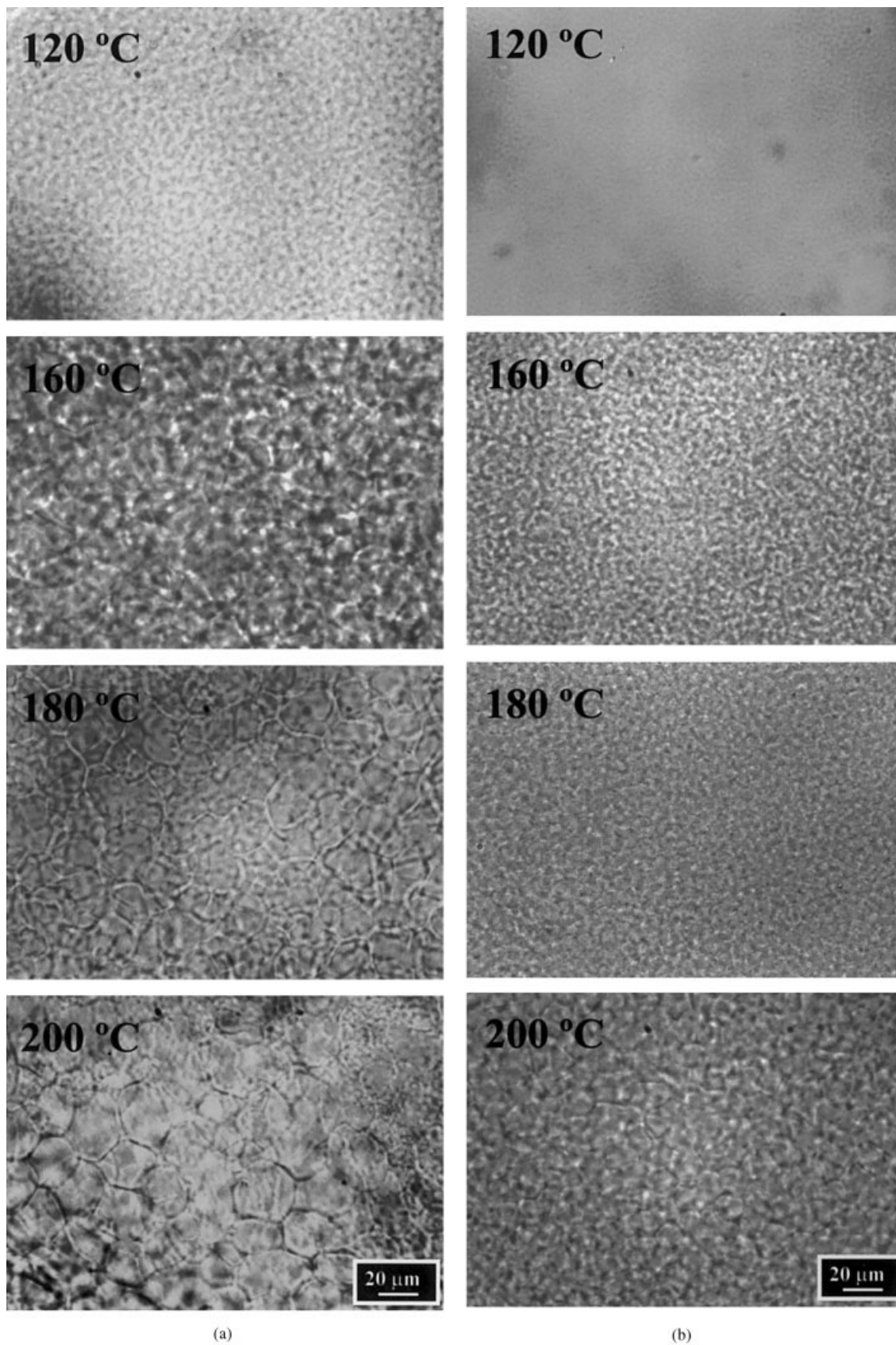
Figure 9   OM micrographs of PSu/MY 790/DDS samples cured at 120, 160, 180, and 200°C that contained (a) 15 and (b) 20 wt % PSu.

bility gap, we find that the only factor that determines the different morphologies is the polymerization rate. This means that, when phase separation begins, the solution viscosities of the two mixtures are similar; but as the cure reaction proceeds, the rate of the viscosity increase is different for the epoxy resins because of differences in the polymerization rate. As we discussed before, the rate of the curing reaction is lower for the DER 332 epoxy resin because of the lower concentration of OH groups. A low solution viscosity during demixing, due to the lower epoxy resin curing rate, facilitated coarsening and coalescence. As a result, the final morphology contained a large area fraction with dispersed PSu domains [see Fig. 8(a)]. However, for the MY 790 epoxy resin, the faster increase in the viscosity, in combination with the nonchanged rate of demixing, resulted in the arrest of phase separation at an earlier stage [see Fig. 8(b)].

The chemical resistance of the plaques was also evaluated by the immersion of the samples in methylene chloride. As expected, the disintegration of the samples in the solvent was dependent on the morphology. For the epoxy continuous morphology, no shape change was observed, but the solvent attacked the PSu continuous-phase sample as soon as the sample was immersed.

Figure 9 shows the variations of the morphology by OM for 15 and 20 wt % PSu-modified MY 790 epoxy resin cured in the microscope at temperatures between 120 and 200°C. The effect of temperature is difficult to analyze. An increase in the cure temperature produces three different effects: an increase in the reaction rate, a decrease in the viscosity, and a decrease in the initial miscibility (LCST). As we discussed in the previous section, the cure temperature has little influence on the miscibility of the system over a wide range of temperatures (Fig. 6). The cure temperature affects the extent of phase separation by fixing the vitrification time of the thermoplastic-rich phase. In samples with 15 wt % PSu cured at 120 and 160°C, a cocontinuous structure was formed. At these cure temperatures, the primary morphology development was arrested at the vitrification of the PSu-rich phase. As a result, demixing was arrested soon. The mobility remained too low, and no evolution of the structure was seen. At high cure temperatures (180–200°C), a continuous PSu-rich phase was obtained, which was indicative of a large extent of demixing.[30] In this case, the demixing gap was already reached at a low conversion corresponding to a rather low epoxy molecular weight and a low solution viscosity. The rate of demixing was high in comparison with the rate of polymerization, and a large extent of demixing was obtained before gelation or vitrification took place. When the initial PSu concentration in the sample was 20 wt % PSu, a cocontinuous morphology was

obtained at all cure temperatures, probably because of the high solution viscosity. The degree of phase separation and the size of the morphology were reduced when either the solution viscosity at the onset of demixing was high (e.g., because of a high PSu concentration) or the cure temperature was low.

CONCLUSIONS

The kinetic behavior of two similar commercial epoxy resins cured with an aromatic diamine was studied.

It was found that PSu had little effect on the kinetics. The presence of the thermoplastic provoked a lower reaction rate of the epoxy–amine species and an increase in the gel times.

Different morphologies were obtained by variations of the PSu concentration, the cure temperature, and the epoxy resin. At concentrations of 5 and 10 wt % PSu, only a random dispersion of PSu-rich particles in an epoxy matrix was formed, whereas above 20 wt % PSu, a cocontinuous morphology was observed for all cure temperatures. For 15 wt % PSu, the final morphology depended on the epoxy resin and the cure temperature selected. The difference in the final morphology between both 15 wt % PSu-modified epoxy resins can be considered to be due to a kinetic factor. The PSu/DER 332/DDS formulation represented a system in which the initial solution viscosity was not changed in comparison with PSu/MY 790/DDS, whereas the rate of the viscosity increase was reduced because of differences in the polymerization rates of the two epoxy resins. Therefore, a high degree of phase separation was expected. As a result, by variations in the rate of the viscosity increase during demixing, different morphologies could be obtained. For curing at low temperatures (120–160°C), demixing took place at a high solution viscosity. As a result, demixing was arrested at an early stage, and a cocontinuous structure was obtained. At high cure temperatures (180–200°C), a large extent of demixing was observed because of the low solution viscosity, and a continuous PSu phase was obtained.

References

1. Raghava, R. S. J Polym Sci Part B: Polym Phys 1987, 25, 1017.
2. Raghava, R. S. J Polym Sci Part B: Polym Phys 1988, 26, 65.
3. Hourston, D. J.; Lane, J. M. Polymer 1992, 33, 1397.
4. Cho, J. B.; Hwang, J. W.; Cho, K.; An, J. H.; Park, C. E. Polymer 1993, 34, 4832.
5. Bucknall, C. B.; Gilbert, A. H. Polymer 1989, 30, 213.
6. Hedrick, J. L.; Yilgor, I.; Jurek, M.; Hedrick, J. C.; Wilkes, G. L.; McGrath, J. E. Polymer 1991, 32, 2020.
7. MacKinnon, A. J.; Jenkins, S. D.; McGrail, P. T.; Pethrick, R. A. Polymer 1993, 34, 3252.
8. Min, B. G.; Stachurski, Z. H.; Hodgkin, J. H. J Appl Polym Sci 1993, 50, 1511.
9. Mackinnon, A. J.; Pethrick, R. A.; Jenkins, S. D.; McGrail, P. T. Polymer 1994, 35, 5319.

10. Huang, P.; Zheng, S.; Huang, J.; Guo, Q. Polymer 1997, 38, 5565.

11. Guo, Q.; Huang, J.; Li, B.; Chen, T.; Zhang, H.; Feng, Z. Polymer 1991, 32, 58.

12. Iijima, T.; Tochiomoto, T.; Tomoi, M. J Appl Polym Sci 1991, 63, 311.

13. Yee, A. F.; Pearson, R. A. Polym Mater Sci Eng 1990, 63, 311.

14. Oyanguren, P. A.; Frontini, P. M.; Williams, R. J. J.; Girard-Reydet, E.; Pascault, J. P. Polymer 1996, 37, 3079.

15. Oyanguren, P. A.; Frontini, P. M.; Williams, R. J. J.; Vigier, G.; Pascault, J. P. Polymer 1996, 37, 3087.

16. Oyanguren, P. A.; Riccardi, C. C.; Williams, R. J. J.; Mondragón, I. J Appl Polym Sci 1998, 36, 1349.

17. Oyanguren, P. A.; Galante, M. J.; Andromaque, K.; Frontini, P. M.; Williams, R. J. J. Polymer 1999, 40, 5249.

18. Galante, M. J.; Oyanguren, P. A.; Andromaque, K.; Frontini, P. M.; Williams, R. J. J. Polym Int 1999, 48, 642.

19. Oyanguren, P. A.; Aizpurua, B.; Galante, M. J.; Riccardi, C. C.; Cortázar, O. D.; Mondragón, I. J Polym Sci Part B: Polym Phys 1999, 37, 2711.

20. Martinez, I.; Martin, M. D.; Eceiza, A.; Oyanguren, P. A.; Mondragón, I. Polymer 2000, 41, 1027.

21. Verchère, D.; Sautereau, H.; Pascault, J. P.; Riccardi, C. C.; Moschiar, S. M.; Williams, R. J. J. Macromolecules 1990, 23, 725.

22. Riccardi, C. C.; Adabbo, H. E.; Williams, R. J. J. J Appl Polym Sci 1984, 29, 2481.

23. Barton, J. M.; Greenfield, D. C.; Hodd, K. A. Polymer 1992, 33, 1177.

24. Fasce, D. P. Thesis, University of Mar del Plata, 1999.

25. Auad, M. L.; Frontini, P. M.; Borrajo, J.; Aranguren, M. I. Polymer 2001, 42, 3723.

26. Girard-Reydet, E.; Riccardi, C. C.; Sautereau, H.; Pascault, J. P. Macromolecules 1995, 28, 7599.

27. Bonnet, A.; Pascault, J. P.; Sautereau, H.; Taha, M.; Camberlin, Y. Macromolecules 1999, 32, 8517.

28. Gordon, M.; Taylor, J. J Appl Chem 1952, 2, 493.

29. Graaf, L. A.; Hempinius, M. A.; Möller, M. Polym Prepr (Am Chem Soc Div Polym Chem) 1995, 36, 787.

30. Graaf, L. A. Thesis, University of Twente, 1994.