Fracture Toughness of Epoxy Resins Modified with Polyethersulfone: Influence of Stoichiometry on the Morphology of the Mixtures

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ABSTRACT: Toughened mixtures containing 15 wt % polyethersulfone were made with diglycicdyl ether of bisphenol-A resin and 4,4′-diaminodiphenylmethane curing agent, with amine/epoxy group stoichiometric ratios varying from 0.6 to 1.5. Fracture behavior of the modified mixtures has been investigated as a function of the stoichiometry in the matrix. Morphology has been analyzed by transmission and scanning electron microscopy. The increase of amine content in the matrix results in a further increased fracture toughness. This behavior has been related to the changes on the ductility of the matrix upon stoichiometric ratio, but also to the changes on microstructural features of the modified mixtures as stoichiometric amine/epoxy group ratio increased. These morphological changes have been interpreted in terms of spinodal decomposition during curing of the epoxy matrix. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 183–191, 1998

Key words: epoxy mixtures; stoichiometry; polyethersulfone; morphology; toughness

INTRODUCTION

Epoxy resins are the most widely used thermosetting polymers for high-performance applications, such as matrices for fiber-reinforced composites and structural adhesives. They have some excellent properties for these applications, but their major drawback is their brittleness. These resins are frequently toughened by the incorporation of a secondary rubbery phase that separates from the matrix during curing, leading to different morphologies.[1–4] Because the addition of rubbers to epoxy resins also leads invariably to significant drops in elastic modulus and in-service temperature,[5–8] in the latter years high-performance thermoplastics have also been used to toughen thermosetting resins[9–13] because of their high modulus and glass transition temperature.

Despite the modest improvements in fracture properties obtained for the thermoplastic-modified mixtures, one of the most studied thermoplastics for the modification of epoxy resins is the poly-(ether sulfones)(PESs).[9,13–24] However, enhancement of fracture behavior of the modified mixtures seems to be closely related to the generated morphologies.[13,25,26]

Although some controversy still exists about the mechanisms of phase separation, with most of the authors claiming that the second phase separates from the epoxy matrix *via* spinodal decomposition.[16,25] In the case of thermoplastic modification, the mixture usually exhibits a lower critical solution temperature (LCST), which permits spinodal decomposition induced by the increase in the molecular weight of epoxy chains through curing. Fixation of morphology in the modified resin will depend on the conditions of cure, the concentration of thermoplastic in the resin, and the materials used.[12,16,26–28] PESs have been shown to present LCST-type phase behavior when mixed with epoxy resins,[15,16,21] so their modified
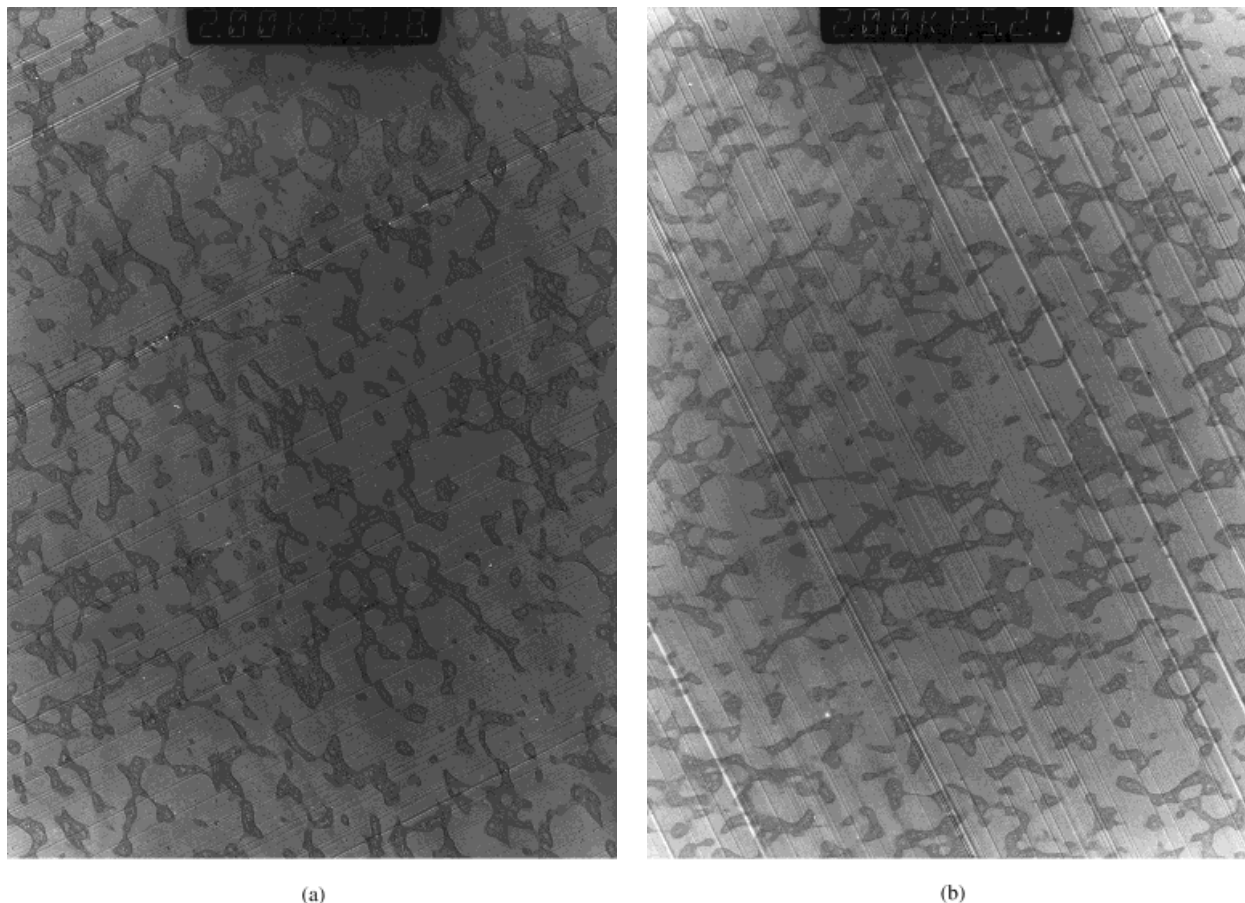
Figure 1   TEM micrographs for stoichiometric mixtures precured at 80°C. (a) 80°–110°C. (b) 80°–110°–140°C. (c) 80°–110°–140°–200°C.

epoxy mixtures are susceptible to present microstructures ranging from spherical particles to cocontinuous two-phase structures.

This article deals with the toughening of a bifunctional epoxy resin modified with a commercial PES at a low concentration. Currently, there are ways to influence the amount of modifier in the epoxy matrix, but there are fewer ways to change the stoichiometric ratio in the matrix. Therefore, in this study, mechanical and fracture toughness results are related to the microstructures generated as a function of the starting amine/epoxy stoichiometric ratio in the epoxy mixture.

EXPERIMENTAL

The epoxy resin used in this study was diglycidyl ether of bisphenol-A (DGEBA), with $n = 0.03$, DER 332, gently supplied by Dow Chemical. The curing agent, 4,4′-diaminodiphenylmethane (DDM), previously used in phase-separation studies with PES,[15,16,19–21] was obtained from Ciba-Geigy. Mixtures were made at various stoichiometric ratios, r, between 0.6 and 1.5, where "r" is defined as $4A/2E$, with A and E being the number of moles of diamine and diepoxide, respectively. PES was Victrex 3600P, kindly donated by ICI plc, which has an $M_n = 14{,}500$ and a polydispersity of $M_w/M_n = 2.60$, as measured by gel permeation chromatography with polystyrene standards. The blending procedure between DGEBA and PES, and further with DDM, has been reported in a previous article[21] in which temperatures and times were used in the full cure schedule to obtain completely cured plaques of 6 mm thickness.

Dynamic mechanical analysis procedures have also been previously reported.[21] Transmission electron microscopy (TEM) measurements have been performed using a Philips CM20 transmission electron microscope, with an accelerating voltage of 120 kV. For these studies, ultramicrotomed films have been cut from the cured plaques with a diamond knife.

(c)

Figure 1 (*Continued from the previous page*)

Scanning electron microscopy (SEM) studies have been performed with an ISI/ABT 55 scanning electron microscope, with an accelerating voltage of 10–15 kV, by using fracture surfaces obtained from flexural tests. Before testing, samples were coated with a gold sputterer. Epoxy-rich mixtures were studied without etching the samples. For amine-rich compositions, etching was made maintaining the specimens with methylene chloride in a Soxhlet for 24 h.

Fracture toughness of these mixtures has been determined using an Instron model 4206 mechanical testing machine, under conditions specified by the European Group on Fracture Task Group.[29] The same machine was used to determine the flexural properties by using conditions specified in ASTM D-790 standard.

RESULTS AND DISCUSSION

Before studying the 15 wt % PES-modified epoxy mixtures prepared with several amine/epoxy stoi-

chiometric ratios, the morphology of the PES-modified stoichiometric mixture has been analyzed by TEM and dynamic mechanical thermal analysis. The morphologies obtained for the PES-modified stoichiometric mixture processed with several cure schedules, all of them having as a common feature the starting at 80°C, are presented in Figure 1. There are no remarkable differences among these micrographs, which show almost interconnected second-phase microstructural domains and also some spherical particles. It is worthwhile to note that small-sized epoxy inclusions appeared within the second-phase particulate/cocontinuous microstructure for all cure schedules used.

Phase separation in the same epoxy–PES mixture has been previously studied for stoichiometric blends with different PES contents.[20,21] The system exhibited a LCST behavior that shifted to lower temperatures as molecular weight of the resin increased through curing. As shown in a previous article, dynamic mechanical properties of these PES-modified stoichiometric mixtures cured with several cure schedules—starting from stages with different temperatures—showed a dissimilar behavior function of the early cure stage temperature.[21] Loss peak temperature data from that paper are shown in Figure 2. The PES-modified mixtures exhibited an increasing compatibility as a lower early cure temperature was used. Higher cure temperatures caused phase separation to occur much before than gelation. On the contrary, for the 80°C early cure stage, the spinodal decomposition began around gelation, thus leading to a lower degree of demixing as
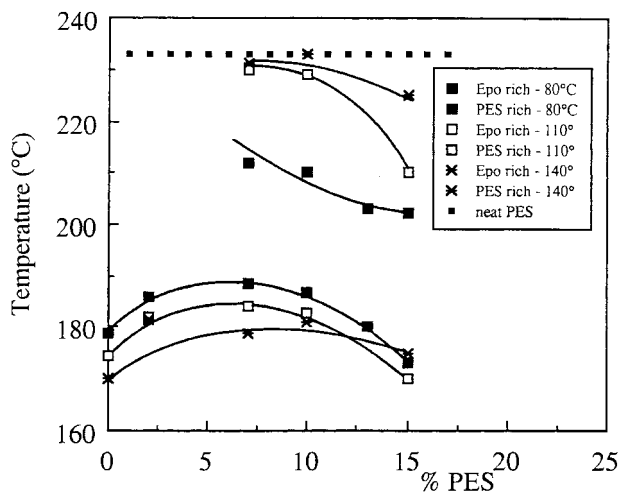

Figure 2 Loss peak temperatures for the modified mixtures precured at different temperatures, compared with that for the loss peak of neat PES. Epo, epoxy.
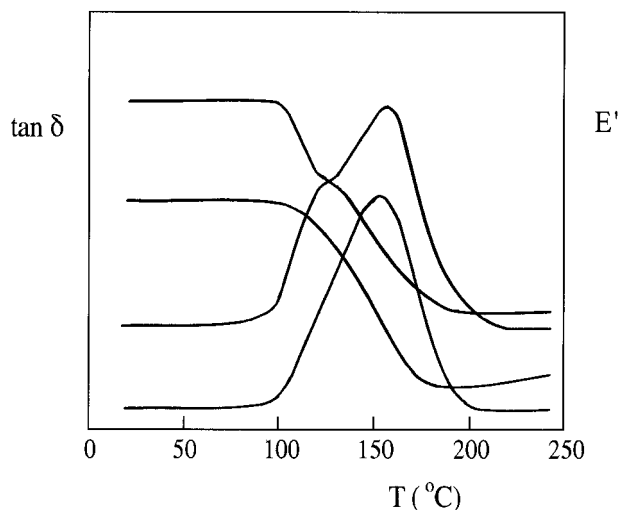
Figure 3 Dynamic mechanical behavior of the modified and neat mixtures cured at 80°–110°C.

these mixtures showed partial miscibility during the early stages of phase separation.

Therefore, after following Inoue's studies[15,16] that indicated two-phase structure develops *via* spinodal decomposition, it becomes clear from Figure 2 that the relative ratio between phase separation rate and polymerization rate through curing governs the microstructure formation for these mixtures leading to the almost cocontinuous structure (shown in Fig. 1) for the 15 wt % PES-modified stoichiometric mixture precured at 80°C. This fact was due to cloud point; gelation times were similar. Thus, fixation of the fragmented structures into spherical domains was not possible for this mixture at this precure temperature.

On the other hand, the high compatibility of the 15 wt % PES-modified stoichiometric mixture (even for the blend cured at all) can be deduced from the dynamic mechanical curves shown in Figure 3 for the PES-modified and neat mixtures cured with a 80°–110°C cure schedule. The PES-modified mixture showed a complex α-relaxation

peak, with a shoulder around 120°C in the low temperature region, but the main α-peak appeared at a temperature similar to that for the unmodified mixture (around 158°C), far away from the one obtained for the mixtures cured with the complete cure schedule shown in Figure 2. Consequently, the PES phase α-relaxation would be included in the α-relaxation of the epoxy-rich phase, and the shoulder could correspond to less-reacted epoxy chains, because of hindering of the second phase, that perhaps remained in the epoxy–PES interphase at the used cure conditions. Further postcuring to 200°C[21] increased the α-peak temperatures, T_α, of the PES-rich and epoxy-rich phases to 205°C and 173°C, respectively. This indicates that, although microstructural features were not modified, phase separation progressed in the PES-rich phase as a consequence of more crosslinking reactions at the interphase, besides the completion of crosslinking reactions in the epoxy phase, which conducted the increase of the crosslinking density of the matrix. An alternative, but complementary, explanation could be that the epoxy oligomers trapped in the PES-rich phase as small inclusions, which at completion of the cure schedule could be as much as 52 wt % of the PES-rich phase,[21] would be responsible for the shoulder in the α-relaxation. This shoulder would move towards higher temperatures, as crosslinking reactions progressed inside the epoxy inclusions, thus also increasing the temperature of the α-relaxation corresponding to the PES-rich phase as more epoxy segregated from it.

Partial miscibility for all 15 wt % PES-modified mixtures cured with several amine/epoxy stoichiometric ratios becomes evident when both the T_α's of the epoxy-rich phase and those for the unmodified mixtures are compared at the completion of the cure schedule. As shown in Table I, the α-relaxation of the epoxy matrix in the modified mixtures occurred approximately at the same temperature than in the neat mixtures; so, indi-

Table I   Dynamic Mechanical Properties in the Glass Transition Region for Both Modified and Neat Mixtures

r	0.6	0.8	0.9	1.0	1.1	1.2	1.4	1.5	1.6
T_g (epoxy-rich phase) (°C)	96 170	137	166	193	188	178	159	153	—
T_g (neat epoxy) (°C)	98	132	168	189	186	175	149	—	120
Er (modified mixture) (N m^{-2})	4.8	38	57	92	77	62	49	34	—
Er (neat epoxy) (N m^{-2})	3.9	25	52	91	76	61	39	—	22

Table II Mechanical and Fracture Toughness Properties of the Modified Mixtures

r	0.6	0.8	0.9	1.0	1.1	1.2	1.4	1.5
K_{Ic} (MN m$^{-3/2}$)	0.77	1.23	1.34	1.44	1.54	2.05	—	—
G_{Ic} (J m^{-2})	130	404	584	685	733	1,275	—	—
E (MPa)	3,700	3,115	2,560	2,560	2,720	2,745	—	3,360
σ_f (MPa)	—	159	145	137	142	153	—	187
R (mm mm^{-1})	(0.04)	(0.09)	—	(0.10)	(0.12)	(0.13)	(0.15)	—
	—	0.11	0.10	0.11	0.13	0.15	—	0.15

Strain values in parentheses correspond to the corresponding neat mixtures.

cating that the separated PES-rich phase practically did not modify the crosslink density of the epoxy matrix. This fact was also confirmed by analyzing the variation of rubber modulus, E_r, measured at $T_\alpha + 40°C$, of the modified mixtures. Thus, modified mixtures with a T_α higher than 165°C had similar E_r values to those for the corresponding unmodified mixtures. The slight higher values of E_r for the modified mixtures at compositions far away from stoichiometry probably arises upon the small contribution of the elastic modulus of the thermoplastic at the $T_\alpha + 40°C$ of these mixtures. The similarity on rubber moduli of both kind of mixtures for stoichiometric ratios around 1.0, at completion of the cure schedule, seems to indicate that both epoxy phases (that for the matrix and that for the inclusions in the PES-rich phase) were crosslinked at the same extent for each stoichiometric ratio. In addition, by applying the Fox equation[30] to the T_α's of the PES-rich phase for different stoichiometric ratios, by taking the T_α of the pure PES and that for the corresponding unmodified mixture completely cured, a similar epoxy weight percentage in the PES-rich phase was obtained for all stoichiometric ratios, which indicated that the increasing molecular weight of epoxy resin during curing, and not the amine units, was mainly responsible for phase separation in the crosslinked mixtures.

Furthermore, fracture behavior of the modified mixtures cured with different stoichiometric ratios was also studied. As reported in a previous article,[21] both flexural modulus, E, and flexural strength, σ_f, shown in Table II, reach a minimum at the stoichiometric ratio independently of thermoplastic modification, and the flexural strain increasing because the addition of PES is most evident at high stoichiometric ratios. On the other hand, the deformability, R, of PES-modified mixtures increased as the stoichiometric ratio of the mixture increased.

The increase on both flexural strength but specially deformability of the modified mixtures upon stoichiometric ratio increase had a clear influence on the toughness behavior of the modified mixtures. Thus, as shown in Figure 4, fracture tests revealed an evident continuous increase on both K_{Ic} and G_{Ic}, as the stoichiometric ratio varied from 0.6 to 1.2 for 15 wt % PES-modified mixtures. It becomes evident that, at low stoichiometric ratios (i.e., for epoxy-rich formulations), the brittleness of the matrix controlled the fracture properties. On the contrary, for amine-rich mixtures, the strength increase—obtained as a consequence of PES addition, along with the higher ductility of the matrix because of the plasticization effect of the unreacted amine excess chains and, as shown herein, the microstructural changes—clearly enhanced the critical stress necessary to propagate the crack. The 10-fold increase observed in the strain energy release rate for stoichiometric ratios changing from 0.6 to 1.2 outlines the importance of using an increasing amount of amine to cure the resin.
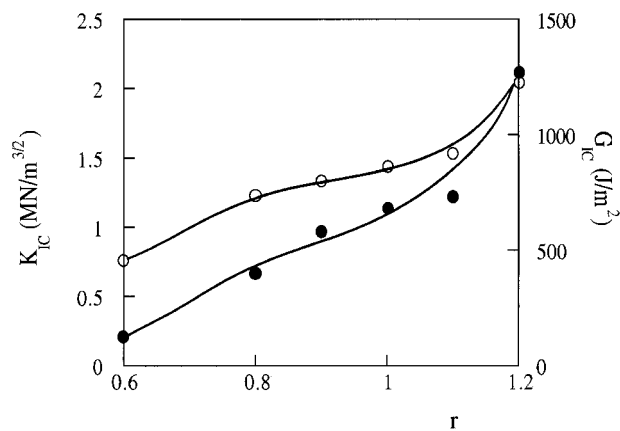
As is well known for thermoplastic- or rubber-

Figure 4 Variation of fracture toughness properties on the stoichiometric ratio.
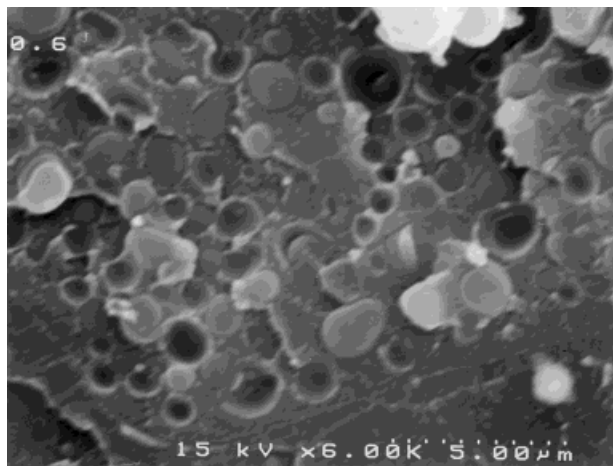
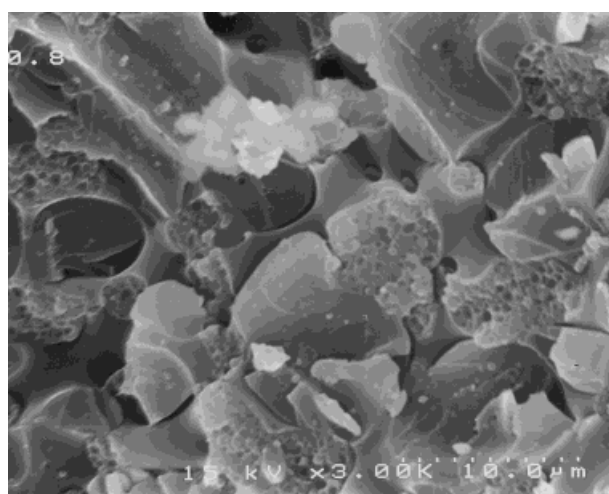**Figure 5** SEM micrograph for the modified mixture with $r = 0.6$.

modified thermosetting resins,[4,12,16,26–28,31] variations in fracture toughness can be directly related to the morphologies of the cured mixtures, which depend on the conditions used for the spinodal decomposition. Thereby, a microstructural study of PES-modified mixtures was conducted by scanning and transmission electron microscopies.

SEM analysis without etching was made to visualize the resulting morphologies of PES-modified epoxy-rich mixtures. Micrographs for the mixtures with $r = 0.6$ and 0.8 are shown in Figures 5 and 6, respectively. For $r = 0.6$ mixtures, nearly spherical domains of a PES-rich phase, with a size ranging from 0.2 to 2 μm diameter, were dispersed in a continuous epoxy phase, appearing as a well-defined boundary between particles and matrix. Thus, these PES rigid spherical particles were not able to steady the fracture at the boundary of the second phase. Microstructural features for the $r = 0.8$ PES-modified mixture were completely different because, as shown in Figure 6(a, b), besides some nonspherical domains with sizes between 0.5 and 6 μm, inhomogeneous regions—possibly corresponding to zones of phase inversion—containing very small spherical inclusions (approximately 0.5 μm domain size) were also observed.

TEM micrographs for $r = 1.0$ (shown herein) and $r = 1.1$ PES-modified mixtures (shown in Figure 7) indicate that microstructural features were changing as the stoichiometric ratio increased, first to a particulate/cocontinuous phase for $r = 1.0$, although a few spherical domains remained and furthermore to a nearly cocontinuous two-phase microstructure, for $r = 1.1$, inside which some phase-inverted regions appeared. As pre-

viously stated,[16] these morphological changes have to lead to toughness increasing as energy absorption at the interphase would be enhanced. From Figures 6 and 7, it becomes clear that the separated PES-rich phase contained an important amount of small epoxy domains, because those (as segregated at the early stage of the cure process) could have a different crosslink density to that for the epoxy matrix, especially if the cure schedule was not completed.

Finally, two-phase mixtures with $r = 1.2$ and 1.5 have also been analyzed by SEM by using methylene chloride-etched samples. Results are presented in Figures 8 and 9, respectively. Figure 8(a, b) shows a practically interconnected globular structure, which in the case for the $r = 1.5$

(a)
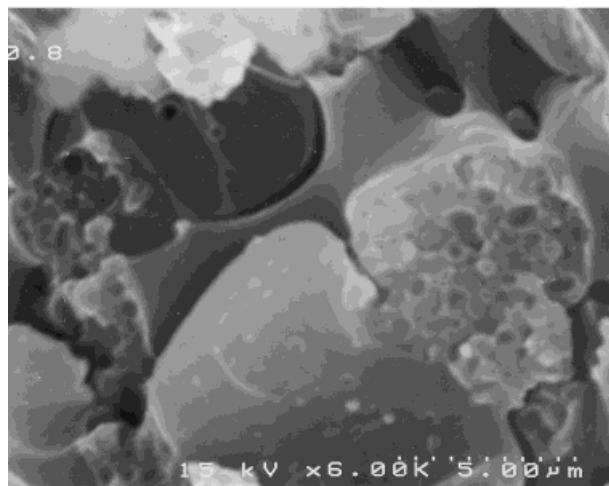
(b)

Figure 6 SEM micrographs for the modified mixture with $r = 0.8$. (a) $3,000\times$ original magnification. (b) $6,000\times$ original magnification.
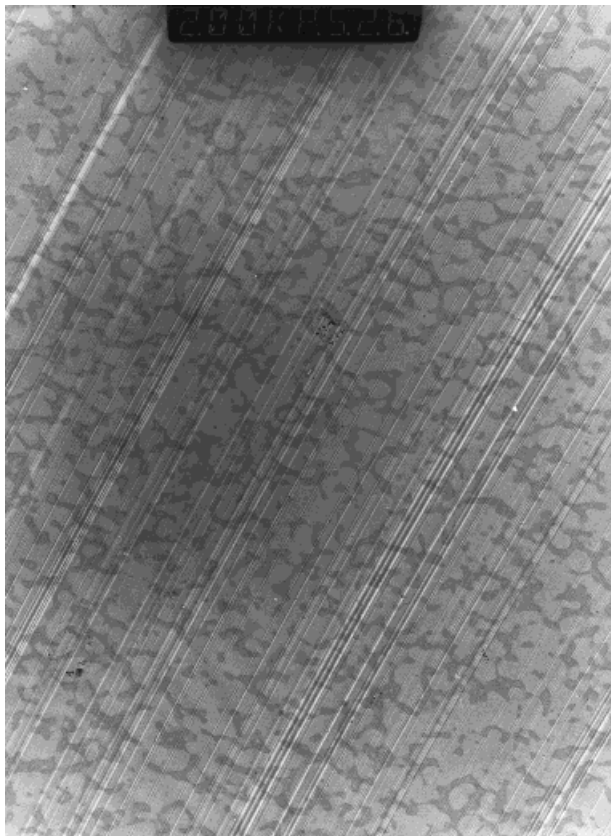
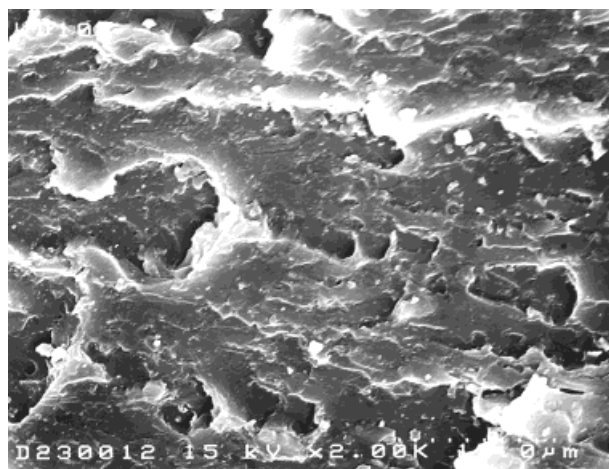**Figure 7** TEM micrograph for the modified mixture with $r = 1.1$.

PES-modifies mixture [Figure 9(a, b)], was even more complex.

The changes in morphology for these 15 wt % PES-modified epoxy mixtures can be explained in terms of phase separation occurring through spinodal decomposition. Thus, by supposing that phase separation happened at around the same curing time independently of the amine amount used, microstructural features for these two-phase mixtures would be dependent on gelation times for the different stoichiometric ratios used. To test the rheology of these mixtures, figure 10 shows the evolution on loss modulus, G'', as a function of curing time at 80°C for unmodified mixtures cured with several curing agent amounts. Gelation times, taken as times at which storage and loss moduli took the same value during curing, or with any other similar criterium, decreased as stoichiometric ratio was higher. Therefore, the ratio between time to phase separation and time to gelation becomes lower as amine content increases in the formulations used or, in another way, the competition progress of phase separation and cure reactions at the cure temperature used in this study was controlled by the rate of polymerization. Thus, microstructural

features of the mixtures were controlled by the amine/epoxy stoichiometric ratio on the mixtures. In this way, a faster cure yielded nearly cocontinuous two-phase structures that led to fracture toughness enhancing. At low stoichiometric ratios, the lower curing rate resulted in the development of an almost monodispersed spherical domain structure.

CONCLUSIONS

In this study, the effect of the variation of the amine/epoxy stoichiometric ratio of the epoxy matrix on the fracture properties of mixtures containing a 15 wt % PES, which showed phase separation on curing, has been studied as a function
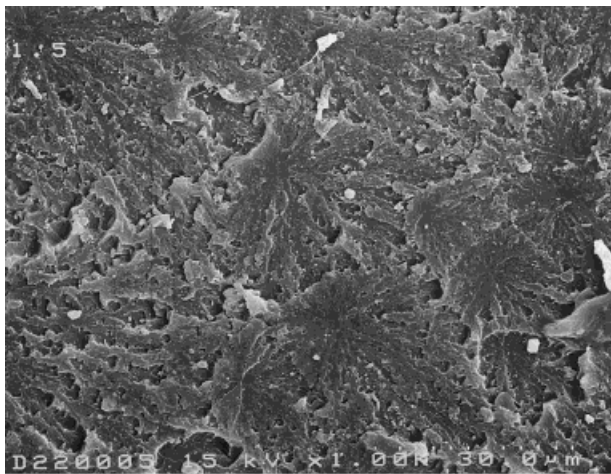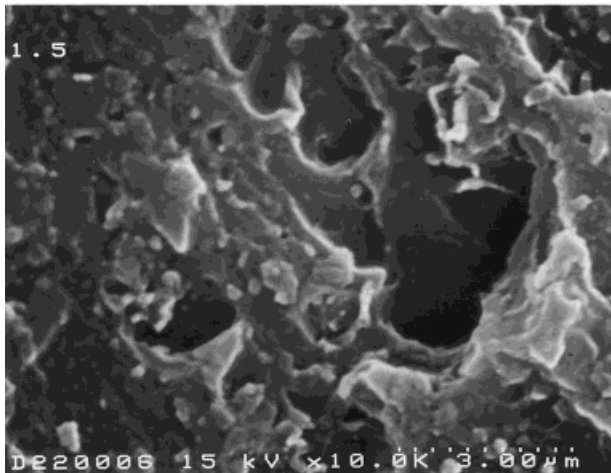

(a)
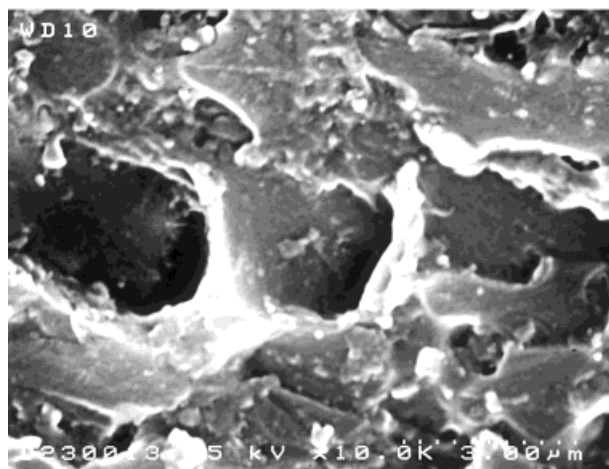
(b)

Figure 8 SEM micrographs for the modified mixture with $r = 1.2$. (a) 2,000× original magnification. (b) 10,000× original magnification.

of the microstructural features of the mixtures. The following conclusions can be drawn:

1. The first stage of the cure schedule used controlled the morphology of the resultant mixture because phase separation and thereafter gelation and vitrification took place in this stage.
2. Fracture toughness increased as the stoichiometric ratio of the epoxy matrix did. This behavior has been related not only to the mechanical properties of the unmodified matrix, but also to the changes occurring in the morphology of the modified mixtures upon stoichiometric ratio of the matrix.
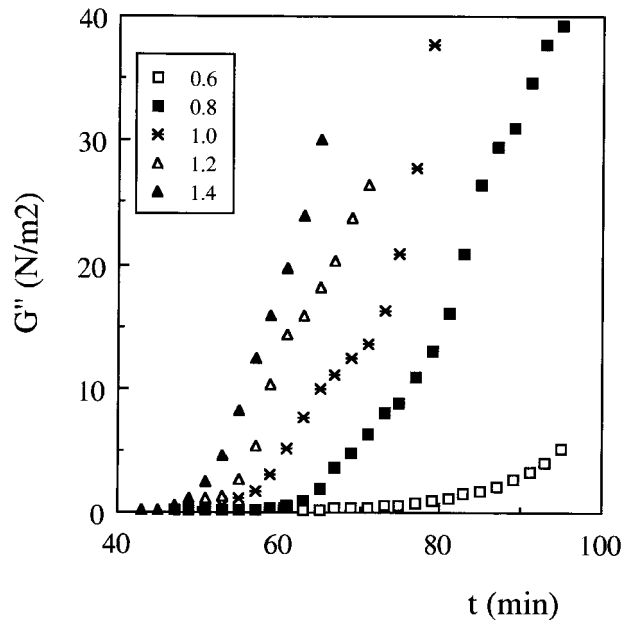3. Phase separation in the modified mixtures,

Figure 10 Evolution of loss modulus through curing at 80°C of the modified mixtures with different stoichiometric ratios.

conducting to microstructural features from spherical particles to a cocontinuous structure as the amine/epoxy stoichiometric ratio increased, has been explained in terms of spinodal decomposition at the early stages of curing.

(a)

(b)

Figure 9 SEM micrographs for the modified mixture with $r = 1.5$. (a) 1,000× original magnification. (b) 10,000× original magnification.

REFERENCES

1. K. Yamanaka, Y. Takagi, and T. Inoue, *Polymer,* **30,** 1839 (1989).
2. C. B. Bucknall, *Toughened Plastics,* Wiley, New York, 1977.
3. S. C. Kunz, J. A. Sayre, and R. A. Assink, *Polymer,* **23,** 1897 (1987).
4. D. Verchere, J. P. Pascault, H. Sautereau, S. M. Moschiar, C. C. Riccardi, and R. J. J. Williams, *J. Appl. Polym. Sci.,* **42,** 701 (1991).
5. T. Iijima, M. Tomoi, J. Yamasaki, and H. Kakiuchi, *Eur. Polym. J.,* **26,** 145 (1990).
6. T. K. Chen and Y. H. Jan, *J. Mater. Sci.,* **26,** 5848 (1991).
7. A. C. Grillet, J. Galy, and J. P. Pascault, *Polymer,* **33,** 34 (1992).
8. M. Franco, M. A. Corcuera, J. Gavalda, A. Valea, and I. Mondragon, *J. Polym. Sci.: Polym. Phys. Ed.,* **35,** 233 (1997)

9. C. B. Bucknall and I. K. Partridge, *Polymer,* **24,** 639 (1983).
10. J. L. Hedrick, I. Yilgor, M. Jurek, J. C. Hedrick, G. L. Wilkes, and J. E. McGrath, *Polymer,* **32,** 2020 (1991).
11. C. B. Bucknall and A. H. Gilbert, *Polymer,* **30,** 213 (1989).
12. D. J. Hourston and J. M. Lane, *Polymer,* **33,** 1379 (1992).
13. A. J. MacKinnon, S. D. Jenkins, P. T. McGrail, and R. A. Pethrick, *Polymer,* **34,** 3252 (1993).
14. C. B. Bucknall and I. K. Partridge, *Polym. Eng. Sci.,* **26,** 54 (1986).
15. K. Yamanaka and T. Inoue, *Polymer,* **30,** 662 (1989).
16. T. Inoue, *Prog. Polym. Sci.,* **20,** 119 (1995).
17. R. S. Raghava, *J. Polym. Sci.: Polym. Phys. Ed.,* **25,** 1017 (1987).
18. R. S. Raghava, *J. Polym. Sci.: Polym. Phys. Ed.,* **26,** 65 (1988).
19. G. Qipeng, *Polymer,* **34,** 70 (1993).
20. C. B. Bucknall, C. M. Gomez, and I. Quintard, *Polymer,* **35,** 353 (1994).
21. I. Mondragon, I. Quintard, and C. B. Bucknall, *Plast. Rubber Comp. Proc. Appl.,* **23,** 331 (1995).
22. B. S. Kim and T. Inoue, *Polymer,* **36,** 1985 (1995).
23. B. S. Kim, T. Chiba, and T. Inoue, *Polymer,* **36,** 43 (1995).
24. B. S. Kim, T. Chiba, and T. Inoue, *Polymer,* **36,** 67 (1995).
25. J. P. Chen and Y. D. Lee, *Polymer,* **36,** 55 (1995).
26. A. J. Kinloch, M. L. Yuen, and S. D. Jenkins, *J. Mater. Sci.,* **29,** 3781 (1994).
27. E. Butta, G. Levita, A. Marchetti, and A. Lazzeri, *Polym. Eng. Sci.,* **26,** 63 (1986).
28. S. M. Moschiar, C. C. Riccardi, R. J. J. Williams, D. Verchere, H. Sautereau, and J. P. Pascault, *J. Appl. Polym. Sci.,* **42,** 717 (1991).
29. European Group on Fracture Task Group, *Testing Protocol,* J. G. Williams, Ed., Imperial College, London, 1990.
30. T. G. Fox, *Bull. Am. Phys. Soc.,* **1,** 123 (1956).
31. A. J. Kinloch and D. L. Hunston, *J. Mater. Sci., Lett.,* **6,** 131 (1987).