MATERIALS AND INTERFACES

Effect of Polyethersulfone on the Mechanical and Rheological Properties of Polyetherimide-Modified Epoxy Systems

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The reaction-induced phase separation process of polyethersulfone- and polyetherimide-modified (PES- and PEI-modified) epoxy systems was investigated by using transmission electronic microscopes (TEM) and a rheometry instrument. The morphologies of cured blends alter considerably with the PES content and molecular weight at the same content of total thermoplastics. Compared with the PEI-modified systems, many complex phase separation mechanisms are observed due to the introduction of PES, but similar relationships between melt viscosity change behaviors and morphology developments are observed in the PES-added ternary systems. Dynamic mechanical analysis (dma) and mechanical studies show that neither heat resistance nor toughness of the resultant blends is obviously influenced by the addition of PES.

1. Introduction

Epoxy resins have been widely used in the electronics industry and fiber-reinforced composites due to their superior thermal, mechanical, and electrical properties such as high tensile strength and modulus, dimensional and thermal stability, and excellent chemical and solvent resistance. Unfortunately, they tend to have a characteristic low resistance to brittle fracture. The improvements in fracture toughness of earlier rubber-modified epoxies are invariably accompanied by a significant drop in stiffness; as a result, much work has been done to toughen highly cross-linked thermosetting polymers with high modulus, high glass transition temperature thermoplastics, such as polyethersulfone (PES),[1,2] polysulfone (PSF),[3] poly(ether ether ketone) (PEEK),[4] and polyetherimide (PEI).[5,6]

Since the mechanical properties of the materials are determined by their final morphologies, much work has been focused on phase separation and morphology control.[7−10] Pascault and co-workers[11] used PEI (Ultem 1000) to toughen epoxy resin and found that effective improvement in toughness is obtained only at high fractions of the engineering thermoplastic, where the thermoplastic forms a continuous phase with the epoxy spherical domain, or the thermoplastic and epoxy form a co-continuous phase. Similar results were also reported by other authors.[12,13] Thus, it is essential to obtain a co-continuous or phase inversion morphology for toughening purposes in material designing and property control.

Inoue and co-worker[14,15] suggested that the spinodal decomposition (SD) mechanism be most conceivable in thermoplastic-modified thermoset systems during the curing process due to the slow rate of nucleation growth (NG). However, it has been found recently[16−20] that viscoelastic effects play a crucial role in the blends with "dynamic asymmetry", and the phase separation process may be determined by the phase diagram and the ratio between the fluctuation growth rate of phase structure and disentangle rate of the polymer chain whatever the phase separation mechanisms, that is, SD and NG. The dynamic asymmetry between constituent components in mixtures or solutions causes a coupling between stress and diffusion which, due to a difference in stress division, induced the abnormal phase structure with threadlike phase inversion morphology.

In our previous works,[7−10] a novel series of PEIs are synthesized and added into epoxy resin to study the phase separation process. Different morphologies are obtained by changing the chain structure and molecular weight of PEI, varying curing temperatures and curing agents. However, phase inversion is obtained only when the content of PEI exceeds a specific weight fraction and the wide application of PEIs is limited by their high price. One solution to this problem is to introduce a lower price thermoplastic toughener into the blend so that PEI content can be lowered, which may serve as a feasible way to broaden the application of this PEI and other high-performance materials alike. Therefore, in part of this work, a hydroxyl-terminated polyethersulfone was added into the epoxy resin as a second toughener and the phase separations and morphologies of the blends were studied for improving material properties.

2. Experimental Section

Materials and Sample Preparation. The epoxy oligomer used, DER 331, was provided by Dow Chemical Co. and is a low molecular weight liquid diglycidyl ether

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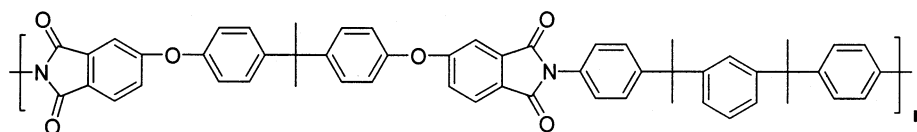
Scheme 1.   PEI

Table 1. Composition of Epoxy Blends (phr Means Parts per Hundred Resin)

blend code	DER 331 (phr)	PEI (phr)	PES-93 (phr)	PES-45 (phr)	DDS (phr)
PEI-14	100	14	0	0	31
PEI-20		20	0	0	
PES-93-6		14	6	0	
PES-45-6		14	0	6	
PES-93-8		12	8	0	
PES-45-8		12	0	8	

of bisphenol A (DGEBA) with an epoxide equivalent of 182−192. Polyetherimide was synthesized by a one-step method from bisphenol A dianhydride (BISA-DA) and 4,4-[1,3-phenylenebis(1-methylethylidene)]bisaniline in *m*-cresol at 200 °C for 6 h. The number-average molecular weight is 2.9×10^4 g/mol and the inherent viscosity is 1.01 dL/g (in 1-methyl-2-pyrrolidinone solvent at 30 °C) (T_g = 218 °C). Two hydroxyl-terminated polyethersulfones (PESs) were supplied by Jilin University, China. PES-45 has a number-average molecular weight of 4.5×10^3 g/mol (T_g = 157 °C) and PES-93 9.3×10^3 g/mol (T_g = 188 °C). The aromatic amine used as a hardener is 4,4′-diaminodiphenyl sulfone (DDS) from Shanghai Third Reagent Factory. The chemical structure of PEI is illustrated in Scheme 1:

The homogeneous mixture of PEI/PES/DGEBA was prepared by adding PEI and/or PES to the stirring epoxy resin at 150 °C under nitrogen gas for 1 h. After the mixture had cooled to 100 °C, a stoichiometric amount of hardener, that is, 31 phr (parts per hundred resin) of DDS, was added and stirred vigorously for 2 min until DDS was completely dissolved; the samples were degassed under vacuum for another few minutes afterward. The mixture was then cast immediately onto glass slides or steel molds, respectively. For comparison, six blends were studied in this work as listed in Table 1. Cure cycles for studying the mechanical or dynamic property were selected as 150 °C for 5 h and postcured at 200 °C for 3 h, or 180 °C for 3 h and postcured at 200 °C for 3 h.

Measurements. A Setaram differential scanning calorimetry (DSC92) instrument was used for T_g detection. Hitachi model S-520 scanning electronic microscopes (SEM) were employed to examine morphologies of the fracture surfaces of cured specimens. For a transmission electron microscopy (TEM) experiment, ultrathin (about 70∼90 nm) sections of blends cured at 150 °C for different times were prepared and observed on a JEM-1200EX TEM instrument. The melt viscosity variations of the blends during cure reaction were recorded on an Ares-9A rheometry instrument: about 1 g of the blend was sandwiched between two circular plates and softened at 80 °C for 2 min. The plate distance was then adjusted to about 1.5 mm and the temperature was raised quickly at a rate of 100 °C/min to the preset curing temperature. All the blends were tested under a parallel plate mode with a controlled shear strain of 1% and test frequency of 1 Hz to ensure that measurements were performed under dynamic equilibrium conditions.

Molded plates were machined to a size of 40 × 6 × 3 mm. Fracture toughness measurements were performed at 23 °C in the three-point bending mode with a span of 24 mm at a crosshead speed of 0.5 mm/min in compliance with ASTM-790M-86. A NETZSCH DMA 242 was used to measure the dynamic properties. The frequency was fixed at 1 Hz and the scanning rate was 5 °C/min over a wide range of temperature (30−280 °C).

3. Results and Discussion

Effect of PES Molecular Weight and Content on the Morphology. SEM morphologies of fractured surfaces of the six finally cured compositions are shown in Figure 1 (all micrographs were shown with the same magnification). All six micrographs represent different stages in what is essentially a single process: the formation and growth of roughly spherical epoxy-rich domains in a thermoplastic-rich (TP-rich) liquid matrix. In Figure 1a,b, the epoxy-rich domains remain separate at the end of the cure reaction, while in Figure 1c−f, the epoxy domains have begun to break through the membranes of TP-rich material that separate them, to form a co-continuous morphology with different degrees of connectivity. The blend PEI-20 displays an inverted phase structure as shown in Figure 1a, in which spherical epoxy-rich particles of regular diameter, about 3 μm, are separated by a space-filling matrix which forms connected membranes between epoxy domains. And the blend PES-93-6 (Figure 1b) also has an inverted phase structure, but in which the gray-colored irregular epoxy-rich particle, about 3−15 μm, disperses in the white PEI-rich matrix, while both the blend PEI-14 (Figure 1c) and PES-45-6 (Figure 1d) show co-continuous (sandwich) morphologies of different sizes; that is, both PEI/PES-rich phase (white region) and epoxy-rich phase (gray region) form a continuous structure. Blend PES-93-8 led to the formation of a sandwich structure as shown in Figure 1e, while PES-45-8 displays a kind of cellular morphology in which irregularly shaped PEI/PES-rich particles of about 20-μm dimension are dispersed in the epoxy-rich matrix (Figure 1f).

Although the mixture of PES−epoxy oligomer without hardener has lower critical solution temperature (LCST) type phase behavior, and the mixture of the PEI−epoxy oligomer has upper critical solution temperature (UCST) type phase behavior as described in previous papers,[11,21] the blends of three components were homogeneous at the curing temperature, similar to the DSC studies (Table 2), showing only one T_g in all blends, where the higher T_g of PES-45-8 most likely was caused by etherification in the hydroxyl end group of the low molecular weight PES with the epoxide group of the epoxy oligomer, while there is very little etherification in the high molecular weight hydroxyl-terminated PES with epoxy resin.[2]

However, when the curing agent was added to the PEI/PES/epoxy solution, it changed the ternary solution into a quaternary system; the miscibility shown in Table 2 can only be a referential indication for the PEI/PES/epoxy oligomer solutions. Although the curing agent
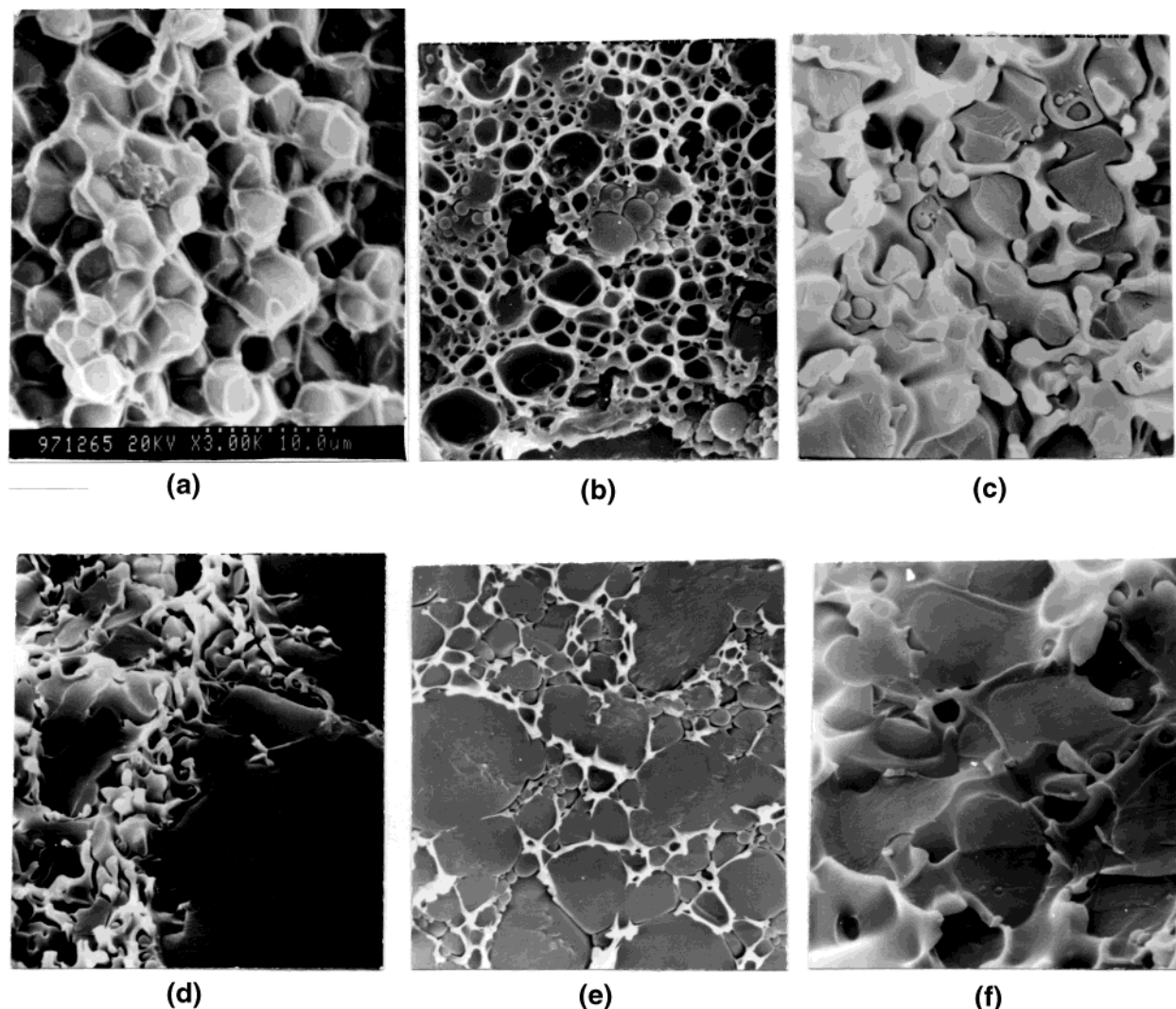
Figure 1. SEM taken on the fractured surface of specimens cured at 150 for 5 h and 180 for 3 h: (a) PEI-20; (b) PES-93-6; (c) PEI-14; (d) PES-45-6; (e) PES-93-8; (f) PES-45-8.

Table 2. DSC Results of Different Blends without Hardener after 24 h at 150 °C

blend code	PEI-20	PES-93-8	PES-45-8
T_g (°C)	18	18	26

could change the miscibility window,[22] no sign of phase separation observed by SEM and light scanning demonstrated that the mixtures were homogeneous solutions before and at the beginning of the curing reaction. As a result, the above morphology change cannot be caused by a second phase separation proceeding after the initial macro-phase separation between PEI and/or PES and epoxy resins before the curing reaction, although the two-stage phase separation process has been observed in ternary blends of epoxy with PES and carboxyl-terminated butadiene-acrylonitrile rubber (CT-BN).[23] Thus, the SEM results show that different morphologies can be achieved by the variation of content or molecular weight of PES to PEI/epoxy/DDS blends.

Rheological Behavior and Phase Structure. In Figure 2 the complex viscosities η^* of three blends were plotted at the same curing temperature. As we can see, at the beginning of the curing reaction, the blends behaved as semidilute polymer solutions having viscosities lower than 5 Pa·s at the curing temperature of 150
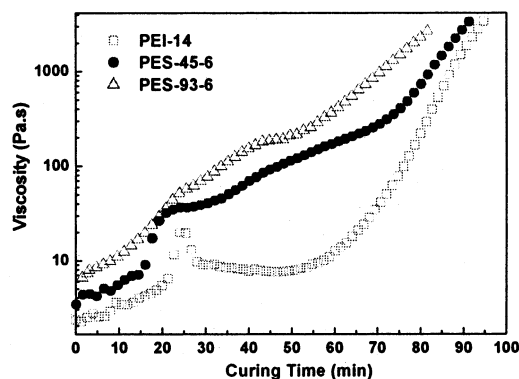

Figure 2. Influence of PES molecular weight on the rheological behavior at 150 °C.

°C. The addition of PES enhanced the initial viscosity, which increased with the enlargement of PES molecular weight.

When phase separation occurred, η^* increased quickly in all three blends. This may be caused by the formation of continuous thermoplastic-rich matrix,[24] which dominated the viscosity of the blends and possessed higher viscosity than the initial viscous solutions.

For PES-93-6 systems, both the molecular weight and volume (weight) fraction of thermoplastic are relatively
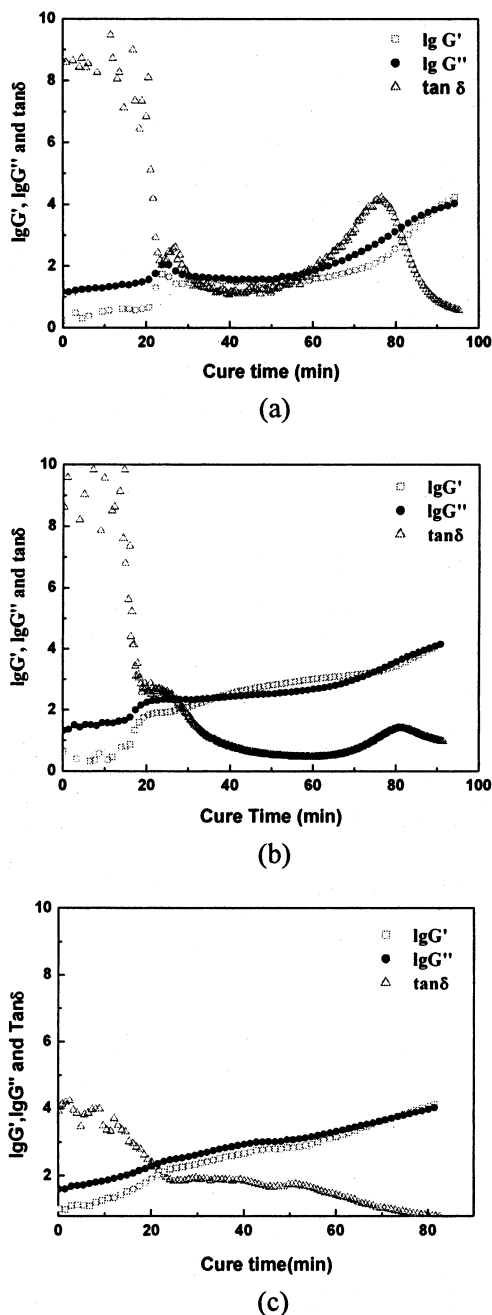
Figure 3. Rheological behavior of the three blends upon curing at 150 °C: (a) PEI-14; (b) PES-45-6; (c) PES-93-6.

high enough to ensure the continuous thermoplastic-rich matrix up to the end of phase separation. As a result, the viscosity increased gradually after the initial phase separation. However, more complex behaviors were observed in the PES-45-6 and PEI-14 systems, which had final sandwich phase structures as shown in Figure 1. After the viscosity jumping at the onset of phase separation, a decrease of viscosity was found that might be deduced by the destroying of the continuous thermoplastic-rich matrix. Similar viscosity changes were also observed and demonstrated to be the result of morphology variation in other thermoplastics-modified epoxy systems as reported in previous works.[24,25]

The modulus of conservation G', modulus of loss G'', and tan δ variation provided information on the onset of phase separation and gelations. The onset of phase separation observed in Figure 3 as dramatic changes in G', G'', and tan δ corresponded well with the viscosity

Table 3. Onset of Phase Separation Time of Four Blends Cured at 150 °C Detected by TRLS and Rhoemetry

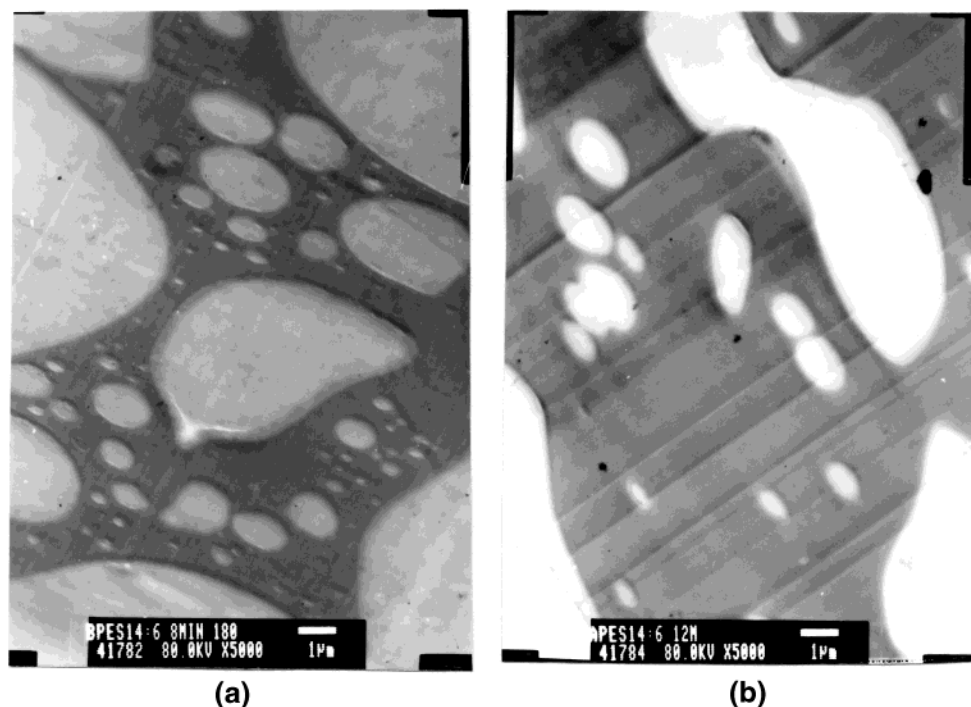| blends	PEI-14	PEI-20	PES-45-6	PES-93-6
t_0 (min) by TRLS	24	23	29.5	28
t_0 (min) by rheometry	22	21	12	8

change in Figure 2. Compared with the blend of PEI-14, both the presence of an additional polymer (PES) and increase of PES molecular weight occurred prior to the onset of phase separation. At this point, in all three blends the formation of a PEI/PES-rich matrix dominated the intensity decrease of tan δ and the increase of conservation modulus G' and of loss modulus G''; however, a small peak of tan δ was observed after the onset of phase separation in the two blends with final sandwich morphology (Figure 3a,b) while a similar phenomenon was not detected in the blend of PES-93-6 with final inversed phase structure (Figure 3c). The peaks of tan δ corresponded with the drop of viscosity as shown in Figure 2, that is, the formation of an epoxy-rich matrix was accompanied by the increase of tan δ and drop of viscosity.

Phase Separation Mechanism. There is a significant difference at the time of onset of phase separation between the results of time-resolved light scattering (TRLS) and rheological measurements (as shown in Table 3). For the blend of PEI-14 and PEI-20, both the TRLS and rheological results show the same onset of phase separation of about 20 min, while the addition of PES brings forward the onset of phase separation time of blends detected by rheological measurements, but the onset of phase separation time was delayed as observed by TRLS. To investigate this abnormal phenomenon, TEM was used to detect the phase structures of PES-93-6 at 8 min (onset of phase separation) and PES-45-6 at 12 min (onset of phase separation). Both large irregular domains and small particles of different sizes are observed in these two systems as shown in Figure 4, while no particle was observed in PEI-20 and PEI-14 at the same time, that is, PES-rich and PEI-rich phases could originate from a double-phase separation process at different times by different mechanisms during the polymerization-induced phase separation process. Compared with PEI-14 and PEI-20, PES-93-6 and PES-45-6 might first form the PES-rich domains by a nucleation and growth (NG) mechanism and a second phase separation of PEI-rich domains by a SD mechanism, which was detected by TRLS, since the PES volume fraction was quite low, an irregular structure was detected by TEM, and no light scattering was observed by TRLS in the early stage of phase separation.

The time delay of TRLS could be explained that the difference in refractive index between the dispersed domains and matrix are not large enough to bring about significant light scattering due to the introduction of PES.

Figure 5 is the scattering profile of the three blends with curing time at 150 °C. No scattered light is observed in the early time of curing, indicating a miscibility at the wavelength scale. After different time lags, a scattering peak appears and the intensity goes up, showing that phase separation is initiated by the curing reaction and proceeds to yield a two-phase morphology. It is worth noting that the peak scattering vector q_m, which is defined by[7-10,15]

$$q_m = (4\pi/\lambda) \sin(\theta_m/2) \qquad (1)$$

Figure 4. Transmission electron micrographs of two blends upon curing at 150 °C: (a) PES-93-6, 8 min; (b): PES-45-6, 12 min.

Table 4. Mechanical Properties of Different Blends Cured at 150 °C for 5 h and Postcured at 200 °C for 3 h

blends	neat epoxy	PEI-20	PES-93-6	PES-45-6
E (MPa)	2480 + 40	3010 ± 60	2980 ± 50	3000 ± 50
K_{IC} (MPa·m$^{1/2}$)	0.63	1.05	1.05	1.02
G_{IC} (J/m^2)	159	324	323	350

Table 5. dma Results for Modulus Decay and Loss Peak Temperature of the Three Blends with Different Curing Procedures

| blend	curing procedure	modulus decay temperature T_{md} (°C)	loss peak temperature T_{lp} (°C)
PEI-20	180 °C 3 h	166	188
	180 °C3 h + 200 °C 3 h	180	198
	150 °C 5 h	144	172
	150 °C 5 h + 200 °C 3 h	178	199
PES-45-6	180 °C 3 h	169	191
	180 °C 3 h + 200 °C 3 h	178	199
	150 °C 5 h	140	162
	150 °C 5 h + 200 °C 3 h	179	199
PES-93-6	180 °C 3 h	175	192
	180 °C 3 h + 200 °C 3 h	180	203
	150 °C 5 h	143	171
	150 °C 5 h + 200 °C 3 h	178	199

where λ and θ_m are the wavelength of scattered light in the sample and the peak scattering angle, respectively, shifts toward a smaller angle and then becomes constant for PEI-14 and PES-45-6 (Figure 5a,b), indicating that at first the coarsening up of morphology takes place and then the morphology is fixed. However, q_m for PES-93-6 shifts to a larger angle with curing before it becomes changeless, and a second peak near 2.8 μm^{-1} of stronger intensity, which might correspond to the small PEI/PES particles dispersed in an epoxy-rich phase, was also observed. As q_m is inversely proportional to the interdomain distance,[15] the shift of q_m toward a larger angle indicates that the interdomain distance becomes shorter during phase separation. This decrease in interdomain distance is often found when phase separation proceeds via the nucleation and growth (NG) mechanism because

more particles are formed progressively during phase separation and the particle-to-particle distances will thus be shorter.[26]

Since PEI and PES are immiscible on the segmental level and their blends are not homogeneous,[27] two thermoplastic-rich phases via similar or different phase separation mechanisms are expected. Pascault and co-workers also found a double-phase separation in the polystyrene- and poly(methyl methacrylate)-modified epoxy system.[28] Because PEI-14 and PEI-20 systems via SD[7−10] and the results of TRLS are always believed to be the signs of SD, it might first proceed via a nucleation and growth mechanism due to the low volume (weight) fraction of PES located far away from the critical point for the blends of epoxy with PES and then follow via a spinodal decomposition (SD) mechanism for the PEI/epoxy components.[29]

Mechanical and Thermal Properties. Table 4. shows the effect of PES molecular weight on the fracture toughness of the modified epoxy samples. Although Young's modulus, fracture toughness (K_{IC}), and fracture energy (G_{IC}) did not change markedly with PES molecular weight variations, K_{IC} and G_{IC} jump greatly compared with those of unmodified epoxy resin. Combined with the SEM results, the fracture energy shows a strong relationship between phase structure and toughness. The toughening effect can be significantly improved in the modified systems with sandwich and phase inversion morphologies as previously reported for PEI and other thermoplastics-modified epoxy resins. The addition of PES shows little influence on the mechanical properties of modified systems with a constant thermoplastic weight fraction.

Table 5 presents dynamic mechanical analysis results of thermal properties of PEI/PES/epoxy and PEI/epoxy systems at the same thermoplastic content. Similarly, almost identical thermal properties were observed for the PES-modified PEI/epoxy systems compared with PEI/epoxy blends cured at the same temperature. The loss peak temperature for all six blends is 200 ± 3 °C
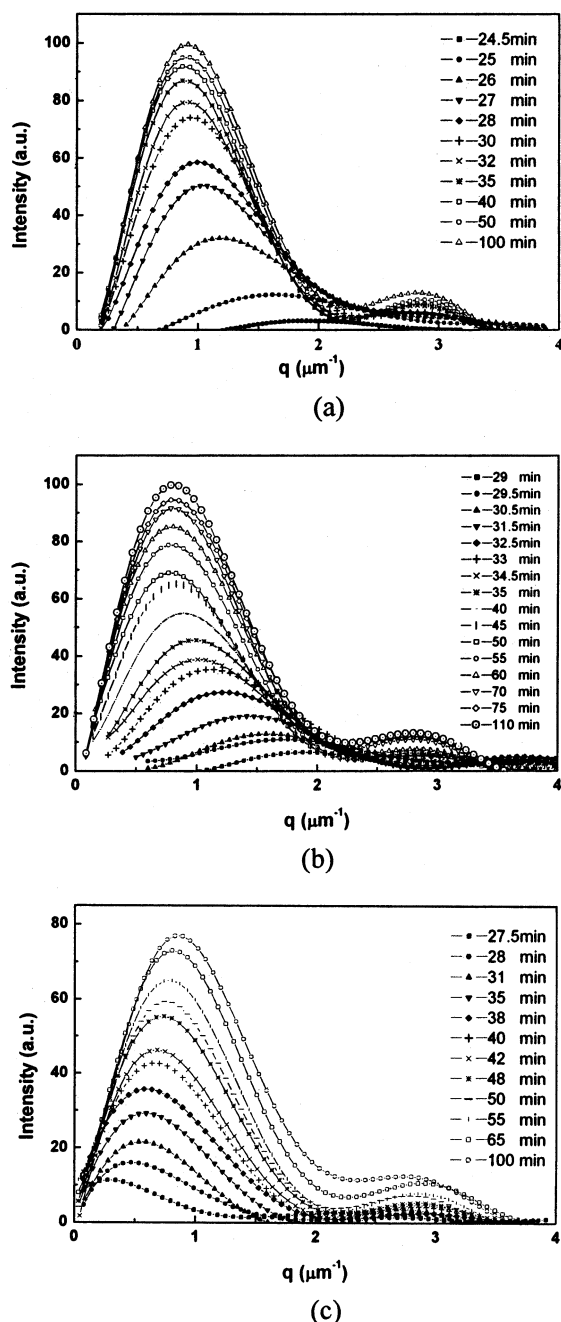
Figure 5. Time-resolved light scattering profiles during curing reaction of three blends at 150 °C: (a) PEI-14; (b) PES-45-6; (c) PES-93-6.

after postcuring because the postcuring temperature in each case was 200 °C, and pure PEI has a T_g that is well above 200 °C, which is the dominant factor in the TP-rich phase rather than the 6% lower T_g PES.

4. Conclusion

Increase of content and molecular weight of PES in the PEI/PES/epoxy three-component systems favors the formation of final continuous thermoplastics-rich phase structure. The behaviors of melt viscosity corresponded well with morphology developments in the PEI/PES/epoxy systems, but many complex phase separation mechanisms are deduced by the introduction of PES. Both mechanical and thermal properties were nearly unchanged by the addition of PES at the same thermoplastics content.

Literature Cited

(1) Bucknall, C. B.; Gomez, C. M.; Quintard, I. Phase-separation from solutions of poly(ether sulfone) in epoxy-resins. *Polymer* **1994**, *35*, 353.

(2) Chen, Y. S.; Lee, J. S.; Yu, T. L.; Chen, J. C.; Chen, W. Y.; Cheng, M. C. The curing reaction of poly(ether-sulfone)-modified epoxy-resin. *Macromol. Chem. Phys.* **1995**, *196*, 3447.

(3) Min, B. G.; Hodgkin, J. H.; Stachurski, Z. H. Microstructural effects and the toughening thermoplastic modified epoxy-resins. *J. Appl. Polym. Sci.* **1993**, *50*, 1065.

(4) Bennett, G. S.; Farris, R. J.; Thompson, S. A. Amine-terminated poly(aryl ether ketone)-epoxy amine resin systems as tough high-performance materials. *Polymer* **1991**, *32*, 1633.

(5) Riccardi, C. C.; Borrajo, J.; Williams, R. J. J.; GirardReydet, E.; Sautereau, H.; Pascault, J. P. Thermodynamic analysis of the phase separation in polyetherimide-modified epoxies. *J. Polym. Sci., Part B: Polym. Phys.* **1996**, *34*, 349.

(6) Bonnet, A.; Pascault, J. P.; Sautereau, H.; Taha, M.; Camberlin, Y. Epoxy-diamine thermoset/thermoplastic blends. 1. Rates of reactions before and after phase separation. *Macromolecules* **1999**, *32*, 8517.

(7) Yu, Y. F.; Cui, J.; Chen, W. J.; Li, S. J. Studies on the phase separation of polyetherimide modified tetrafunctional epoxy resin. II. Effects of the molecular weight. *J. Macromol. Sci. Chem.* **1998**, *A35*, 121. Cui, J.; Yu, Y. F.; Li, S. J. Studies on the phase separation of polyetherimide modified tetrafunctional epoxy resin. III. Morphology development of the blend during curing. *J. Macromol. Sci. Chem.* **1998**, *A35*, 649.

(8) Cui, J.; Yu, Y. F.; Chen, W. J.; Li, S. J. Studies on the phase separation of polyetherimide-modified epoxy resin. 2. Effect of molecular weight of PEI on the structure formation. *Macromol. Chem. Phys.* **1997**, *198*, 3267. Cui, J.; Yu, Y. F.; Li, S. J. Studies on the phase separation of polyetherimide-modified epoxy resin, 3—Part 1—Morphology development of the blend during curing. *Macromol. Chem. Phys.* **1998**, *199*, 1645.

(9) Zhang, Z. C.; Cui, J.; Li, S. J.; Sun, K.; Fan, W. Z. Effect of hydroxyl-terminated polyethersulfone on the phase separation of polyetherimide-modified epoxy resin. *Macromol. Chem. Phys.* **2001**, *202*, 126.

(10) Wu, X. G.; Cui, J.; Ding, Y. F.; Li, S. J.; Dong, B. Z.; Wang, J. Studies on the phase separation of poly(ether imide)-modified epoxy resin, 5—Phase separation behavior of a quasi-binary system. *Macromol. Rapid Commun.* **2001**, *22*, 409.

(11) GirardReydet, E.; Vicard, V.; Pascault, J. P.; Sautereau, H. Polyetherimide-modified epoxy networks: Influence of cure conditions on morphology and mechanical properties. *J. Appl. Polym. Sci.* **1997**, *65*, 2433.

(12) Su, C. C.; Woo, E. M. Cure kinetcs and morphology of amine-cured tetraglycidyl-4,4′-diaminodiphenylmethane epoxy blends with poly(ether imide). *Polymer* **1995**, *36*, 2883.

(13) Cho, J. B.; Hwang, J. W.; Cho, K.; An, J. H.; Park, C. E. Effects of morphology on toughening of tetrafunctional epoxy-resins with poly(ether imide). *Polymer* **1993**, *34*, 4832.

(14) Yamanaka, K.; Inoue, T. Structure development in epoxy resin modified with poly(ether sulphone). *Polymer* **1989**, *30*, 662.

(15) Inoue, T. Reaction-induced phase-decomposition in polymer blends. *Prog. Polym. Sci.* **1995**, *20*, 119.

(16) Araki, T.; Tanaka, H. Three-dimensional numerical simulations of viscoelastic phase separation: Morphological characteristics. *Macromolecules* **2001**, *34*, 1953.

(17) Tanaka, H.; Miura, T. Critical anomaly of complex shear modulus in polymer-solutions viscoelastic suppression of order-parameter fluctuation due to dynamic asymmetry. *Phys. Rev. lett.* **1993**, *71*, 2244.

(18) Tanaka, H.; Araki, T. Phase inversion during viscoelastic phase separation: Roles of bulk and shear relaxation moduli. *Phys. Rev. Lett.* **1997**, *78*, 4966.

(19) Toyoda, N.; Takenaka, M.; Hashimoto, T. Experimental studies of stress-diffusion coupling in semi-dilute polymer solutions. I. 'Viscoelastic length' and viscoelastic effects on early stage spinodal decomposition. *Polymer* **2001**, *42*, 9193.

(20) Tanaka, H. Viscoelastic phase separation. *J. Phys.: Condens. Matter* **2000**, *12*, R207.

(21) Kim, B. S.; Chiba, T.; Inoue, T. Morphology development via reaction-induced phase-separation in epoxy poly(ether sulfone) with functional end-groups. *Polymer* **1995**, *36*, 43.

(22) Pascault, J. P.; Williams, R. J. J. Formulation and characterization of thermoset-thermoplastic blends. In *Polymer Blends*; Paul, D. R., Bucknall C. B., Eds.; John Wiley & Sons: New York, 2000.

(23) Kim, S. T.; Kim, J. K.; Choe, C. R.; Hong, S. I. Multi-phase toughened epoxy with poly(ether sulphone) and carboxyl-terminated butadiene-acrylonitrile rubber. *J. Mater. Sci.* **1996**, *31*, 3523.

(24) Bonnet, A.; Pascault, J. P.; Sautereau, H. Epoxy-diamine thermoset/thermoplastic blends. 2. Rheological behavior before and after phase separation. *Macromolecules* **1999**, *32*, 8524.

(25) Kim, H.; Char, K. Effect of phase separation on rheological properties during the isothermal curing of epoxy toughened with thermoplastic polymer. *Ind. Eng. Chem. Res.* **2000**, *39*, 955.

(26) Kyu, T.; Lee, J. H. Nucleation initiated spinodal decomposition in a polymerizing system. *Phys. Rev. Lett.* **1996**, *76*, 3746.

(27) Guo, Q. P.; Qiu, L. W.; Ding, M. X.; Feng, Z. L. Tensile properties of blends of poly(ether sulfone) with a poly(ether imide). *Eur. Polym. J.* **1992**, *28*, 1045.

(28) Galante, M. J.; Borrajo, J.; Williams, R. J. J.; GirardReydet, E.; Pascault, J. P. Double phase separation induced by polymerization in ternary blends of epoxies with polystyrene and poly(methyl methacrylate). *Macromolecules* **2001**, *34*, 2686.

(29) Elicabe, G. E.; Larrondo, H. A.; Williams, R. J. J. Light scattering in the course of a polymerization-induced phase separation by a nucleation growth mechanism. *Macromolecules* **1998**, *32*, 8173.