STUDIES ON PHASE SEPARATION OF POLYESTERIMIDE-MODIFIED EPOXY RESIN. II. EFFECT OF CURING TEMPERATURE ON PHASE SEPARATION AND ADHESIVE PROPERTY

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ABSTRACT

A sort of polyesterimide (PEsI) was used as a toughening agent in the modification of epoxy resin/anhydride system. The reaction-induced phase separation in amorphous thermoplastic-modified epoxy system was observed *in situ* by means of time-resolved light scattering (TRLS) and advanced rheometric expansion system (ARES) at different curing temperature. TRLS displayed that the phase separation of the blend system followed a spinodial decomposition mechanism at different curing temperature. The increase of curing temperature accelerated curing reaction and the increase of the blend viscosity prevented phase separation from proceeding. Results of TRLS and ARES showed that the phase structure fixation was pinned up by blend viscosity at the early stage of curing reaction, rather than by gelification at the late stage of curing reaction. All the experiments, including scanning electron microscopy (SEM), suggested that low curing temperature was beneficial to the formation of longer interdomain distance of the epoxy-in-rich phase in the blend and to the improvement of adhesive property of the blend.

Key Words: Polyesterimide; Thermosetting; Phase separation; Phase structure; Morphology; Epoxy resin; Toughening agent; Blend; Adhesive property

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INTRODUCTION

Toughening of epoxy resin networks has raised much attention in recent years because epoxy resins possess many excellent properties and are ideal candidates for many important applications. As a traditional toughening agent, reactive rubber was incorporated into the epoxy resin to form a multiphase network during the curing process [1]. However, in this case the toughness enhancement is accompanied with a significant sacrifice of properties at elevated temperature. On the other hand, many thermoplastics, such as polysulfone (PSF) [2], polyethersulfone (PES) [3-6], poly (ether ether ketone) (PEEK) [7-8] and polyetherimide (PEI) [9-15, 26], were also used as toughening agents. The studies have shown that these thermoplastics enhance the toughness without severely sacrificing the properties of epoxy resins. It is also known that these modified epoxy resins are two-phase systems in which the phase separations proceed via spinodial decomposition mechanism induced by an increase of the molecular weight of the epoxy network during the curing reaction [16]. The morphology of these systems, which decides the properties of the modified epoxy resins, is the result of the fixation of the phase-separation structure [17].

Polyesterimides (PEsI) have higher T_g and higher modulus than polyetherimides (PEI) do. Aromatic polyesterimides are witnessed to have an increasing use in aerospace and microelectronic industries because of their outstanding thermal stability and good mechanical strength [18-19]. However, the modification of the epoxy resin with polyesterimide was scarcely reported. A sort of polyesterimide, PEsI-B, was synthesized in our laboratory for toughening epoxy resins. A preliminary study showed that phase separation in the blend system was allowed to proceed to form a two-phase structure via a spinodial decomposition mechanism [20]. With the increase of the PEsI-B content from 0 phr to 40 phr, the phase structure of the cured blend changed from dispersed phase to sandwich phase, and finally to inverted phase. The adhesive properties of the modified epoxy resin were significantly improved due to the addition of PEsI-B.
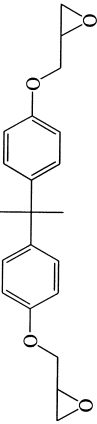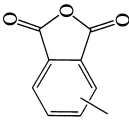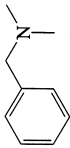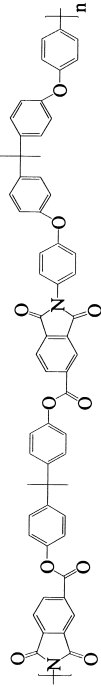
This paper concerns the morphology structure changes in the blend of epoxy resins and PEsI-B with curing temperature. The phase separation process of PEsI-B modified epoxy resin system was traced by means of TRLS and ARES. The morphology of these modified systems was observed by using SEM. Furthermore, the relationship between phase structure and adhesive property of the modified blend was also investigated.

EXPERIMENTAL

Materials and Synthesis of Polyesterimide

The materials used in this work and their schemes are listed in Table 1. The epoxy resin was diglycidyl ether of bisphenol A (DGEBA), DER 331, DOW. DER 331 was treated for removing volatile organic substances under vacuum at 80°C

Table 1. Characteristics of the Different Materials Used

Reactant	Formula	Supplier	M_n (g/mol)	M_w (g/mol)	T_g (°C)
Diglycidyl ether of bisphenol A (DGEBA), n=0.15		Dow Chemicals DER 331	364-380	/	/
Methyl tetrahydrophthalic anhydride (MTHPA)		Ciba Geigy Chemicals	166	/	/
Benzyldimethylamine (BDMA)		Shanghai Chemical Reagent Factory	135	/	/
Polyesterimide (PEsI-B)		Self-prepared	18,000	49,000	216

before use. The curing agent was methyl tetrahydrophthalic anhydride (MTHPA), HY 918, Ciba-Geigy. The accelerator was benzyldimethylamine (BDMA), purchased from the Shanghai Chemical Reagent Factory.

PEsI-B used in this work was synthesized through a polymerization between 2,2'-bis(p-trimellitoxyphenyl) propane dianhydride (BTPDA) and p,p'-bis(p-aminophenyloxy)diphenyl propane (BAPP). 2,2'-bis(p-trimellitoxyphenyl) propane dianhydride (BTPDA), having a melting point of 191°C, was synthesized in our laboratory according to the literatures [21-22]. The diamine, p,p'-bis(p-aminophenyloxy)diphenyl propane (BAPP), was supplied by the Shanghai Institute of Synthetic Resin. 75.00 g (0.1301 mol) of BTPDA was added into a solution of 53.41 g (0.1301 mol) of BAPP in 1000 ml of anhydrous 1-methyl-2-pyrrolidinone (NMP). The reaction mixture was acutely stirred under a nitrogen blanket for 8 houra at room temperature. Acetic anhydride (208 g, 2.04 mol) and triethylamine (11 g, 0.108 mol) were added to the polyamic acid solution. The reaction was kept for 8 hours at room temperature and then for another 1 hour at 80°C. The resultant was precipitated in methanol. The precipitate was mechanically crashed and washed three times with methanol. The polyesterimide was dried for 10 hours at 80°C and then for 4 hours at 200°C under vacuum. Chemical shifts of PEsI-B in HNMR (BRUKER 300, CD_3COCD_3) were at 8.74 (d, 2H, aromatic H), 8.62 (d, 2H, aromatic H), 8.09 (d, 2H, aromatic H), 7.40 (d, 4H, aromatic H), 7.34 (d, 4H, aromatic H), 7.26 (d, 4H, aromatic H), 7.18 (d, 4H, aromatic H), 7.13 (d, 4H, aromatic H), 7.00 (d, 4H, aromatic H), 1.74 (s, 6H, methyl H), 1.71 (s, 6H, methyl H) ppm. The synthesized PEsI-B is an amorphous material having a glass transition temperature (T_g) at 216°C by using DSC (SETARAM 92). The intrinsic viscosity is 0.69dL/g (in NMP at 30°C). The M_w, 49,000 g/mol, of PEsI-B is measured in tetrahydrofuran by using GPC (HP 1100).

Measurements

The samples used in AERS were prepared by dissolving 20 g (100 phr) of DGEBA, 16 g (80 phr) of MTHPA, 8 g (40 phr) of PEsI-B and 0.04 g (0.2 phr) of BDMA in anhydrous chloroform and the solution was diluted to a 30% concentration. About 20 ml of the 30% blend solution was poured into a 10 cm-diameter stainless pan. After a majority of chloroform was vaporized in ambience, the blend was treated under vacuum for 96 hours at room temperature and a semitransparent and semisolid blend was obtained. About 1 g of the semi-solid blend was placed between two 25 mm-diameter parallel plots. The dynamic time sweep at a given temperature, pulsation (1 rad/s), and deformation (1%) and gap (1 mm) was used in order to obtain complex viscosity changes of the blend vs. time on an ARESA4 instrument (Rheometric Scientific, Inc.).

The samples used in TRLS were prepared as the following step. 5 ml of the 30% blend solution above was diluted to a 10% concentration and filtrated with a 3G glass-filter funnel for removing exiguous dust. A drop of the 10% blend solu-

tion was dripped on a piece of clean glass, about 8 mm × 8mm, and chloroform was vaporized under vacuum for 24 hours at room temperature. The sample was covered with another piece of glass. The sample between two pieces of glass was preheated in a heating oven at 80°C for 5 minutes and then quickly pressed into a thin film about 5 μm. The thin film was cured at 110°C, 130°C, and 150°C, respectively. The phase separation behavior was traced at real time and *in situ* on a self-made TRLS instrument with a controllable hot chamber. The TRLS technique was described in detailed elsewhere [24]. After TRLS testing, the cured sample was broken off in liquid nitrogen. The morphology of the fractured surfaces was observed with a scanning electronic microscope (SEM, Hitachi S-520).

The tensile lap-shear strengths of the polyesterimide modified blend were measured according to ISO 4857:1995(e). The 30% blend solution was brushed on several testing panels of aluminum. Chloroform was vaporized for 20 minutes at room temperature. The testing panels were overlapped in pairs and fixed with two steel clips. The samples were pre-cured for 4 hours at 110°C, 130°C, and 150°C, respectively, then post-cured for 10 hours at 150°C. Measurements were carried out with a Shimadzu Autograph DDS-5000 universal testing machine at a speed of 5 mm/min.

To evaluate the bond strength of the PEsI-B modified blends, the 30% blend solution was used as impregnating agent in conjunction with bare aluminum wire substrates. Several helical coils, which had a mandrel diameter of 6.3 mm and a length of 75 mm, were immersed into the impregnating agents consisting of the PEsI-B modified epoxy resin for 60s and then drained for 20 minutes. The impregnated helical coils were pre-cured for 4 hours at 110°C, 130°C, and 150°C, respectively, nd then post-cured for 10 hours at 150°C. Bond strengths were measured with a Shimadzu Autograph DDS-5000 universal testing machine according to IEC 1033:1991 at a speed of 50 mm/min.

RESULTS AND DISCUSSION

Trace of Phase Separation with TRLS

Reaction-induced phase separations in a thermoplastic-modified thermosetting polymer were caused by the increase of the average molar mass of the thermosetting polymer. This process and phase mechanism could be commonly monitored with a TRLS testing. Figure 1 shows the light-scattering profiles at various stages of epoxy/PEsI-B blend curing reactions at 110°C, 130°C, and 150°C, respectively. The epoxy/PEsI-B blend with MTHPA was a single-phase system for all the experiment temperatures, and showed no appreciable light scattering in the early stages of the curing reaction, indicating that PEsI-B could be dissolved in the precursor of DGEBA and MTHPA. After a latent period of 753s, 344s and 274s, corresponding to 110°C, 130°C, and 150°C, respectively, the peak scattering vectors (q_m) emerged and the light scattering intensity went up, implying that
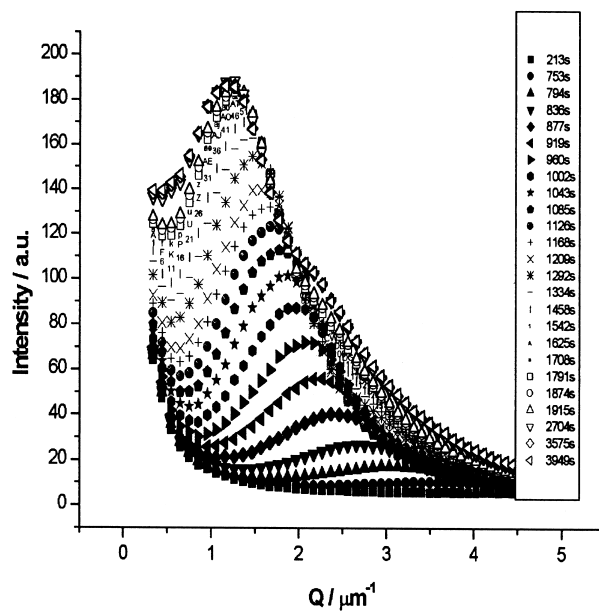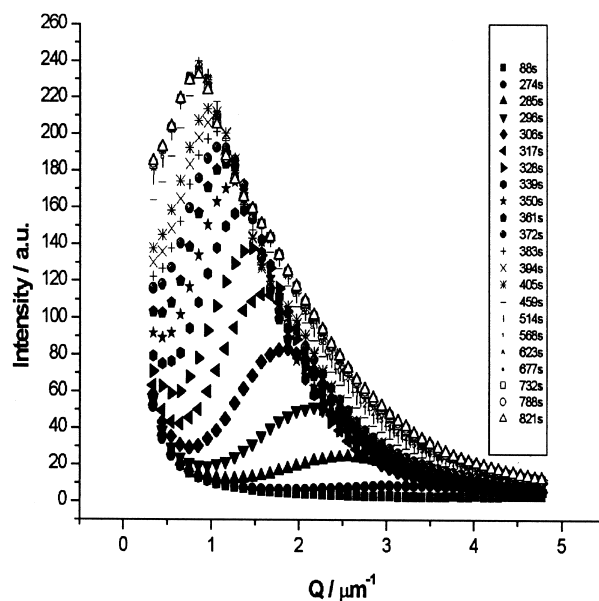
(a)
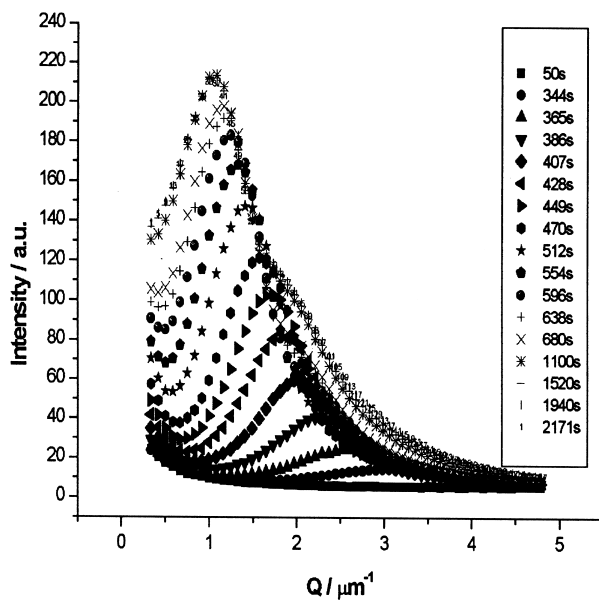
(b)

Figure 1. Change of the light scattering profiles of the blend. (a) Cured at 110°C; (b) cured at 130°C; (c) cured at 150°C.

(c)

Figure 1. Continued.

phase separation was initiated by curing reaction. The time, when the peak scattering vectors (q_m) began to emerge, was usually defined as cloudy point (CP). Here, q_m was the scattering vector defined by $q_m =(4\pi/\lambda)sin(\theta_m/2)$, where λ and θ_m were the wavelength of scattered light and the peak scattering angle respectively. It was also seen that the peak scattering vectors (q_m) first moved from a large angle to a small angle, and finally became steady. The ring patterns and the characteristic changes in scattering profiles indicate that the phase separation of epoxy/PEsI-B blend went through a spinodial decomposition.

To obtain the fixation time (t_{fix}) of the phase structure, the peak scattering vectors (q_m) were plotted as a function of curing time. In Figure 2, the peak scattering vectors (q_m) rapidly decreased with time and then level off upon curing. The t_{fix} was obtained by extending the declining part and leveling part of the peak scattering vector curves. The t_{fix} of the blend were 1004s, 456s and 319s at 110°C, 130°C, and 150°C, respectively, refer to Table 2. With the increase of the curing temperature, the fixation times (t_{fix}) of the phase structure were apparently shortened. In Figure 2, with the process of phase separation, the peak scattering vectors (q_m) of the blends first decreased and finally kept constant, staying at 1.26 μm^{-1}, 1.08 μm^{-1} and 0.87 μm^{-1} (listed in Table 2), corresponding to 110°C, 130°C and 150°C respectively. Because the peak scattering vectors (q_m) had a reciprocal relationship with interdomain distances of epoxy-in-rich phase in the cured blend, a
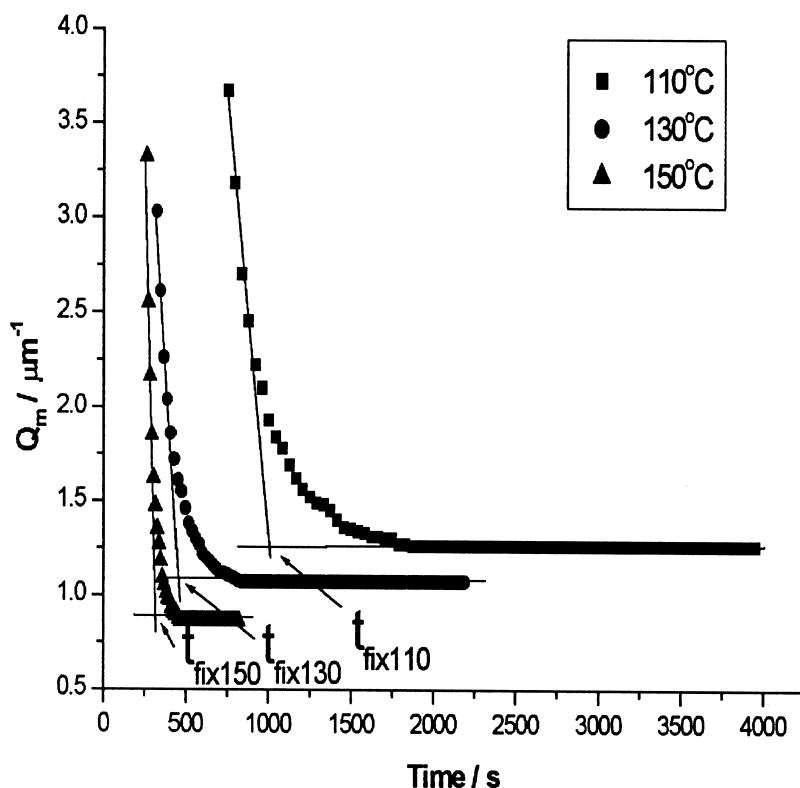
Figure 2. q_m vs. curing time for the blend at different temperatures. (■) 110°C; (●) 130°C; (▲) 150°C.

smaller peak scattering vector (q_m) represented longer average interdomain distance. Figure 2 displays that the increase of curing temperature was beneficial to the formation of longer interdomain distances. In Table 2, cloudy points, phase structure fixation times, and final peak scattering vectors (q_m) of the phase separation process at different temperatures are listed. The increase of the curing temper-

Table 2. Induced Periods of Phase Separation, Phase Structure Fixation Times, Gelation Times, and Stable Peak Scattering Vectors of the Blend at Different Temperatures

| Curing Temperature (°C)	Induced Period of Phase Separation[a] (s)	Phase Structure Fixation Time[a] (s)	Gelation Time[b] (s)	Stable Peak Scattering Vector[a] (μm^{-1})
110	753	1004	1550	1.26
130	344	456	6800	1.08
150	274	319	2000	0.87

[a]Measured in TRLS.
[b]Measured in ARES.

ature accelerates the curing reaction and also rapidly increases the blend viscosity at the same time. The high viscosity of the blend resulted in the advent of the phase structure fixation time. Because PEsI-B hadn't enough time to separate from the blend, epoxy-in-rich phases were surrounded by a comparatively smaller amount of continuous polyseterimide in-rich phase. So the average interdomain distances of the epoxy-in-rich phase in the blend appeared at a longer length in the blend with the same composition.

Observation of Morphology with SEM

The TRLS sample was fractured in liquid nitrogen and the morphology of the fractured surface was observed by using SEM. In the previous study, the white region was confirmed as PEsI-B-in-rich phase, and the dark region represented epoxy-in-rich phase. Figure 3 shows that the curing temperature had significant influences on the average interdomain distances of the epoxy-in-rich in the blend.
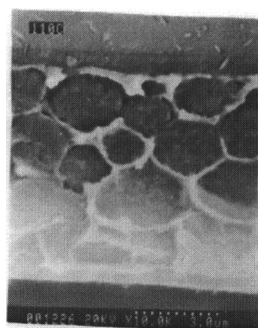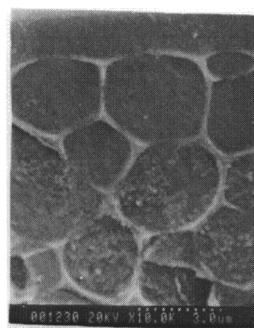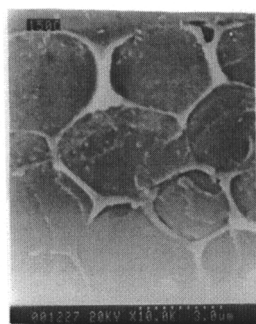
Figure 3. SEM micrographs of the 40 phr blends cured at different temperatures. (a) 110°C; (b) 130°C; (c) 150°C (magnification × 5000).

The result of SEM coincided with the conclusion by TRLS. A lower curing temperature was beneficial to the formation of a shorter phase interdomain distance.

Trace of Complex Viscosity with ARES

Changes in complex viscosity of the blend during isothermal curing were monitored by using ARES. In Figure 4, which is the curve of complex viscosity of the DGEBA/PEsI-B blend with MTHPA vs. curing time at 110°C, 130°C, and 150°C, respectively, the complex viscosity of the blend slowly increased at the early stage of the curing reaction. After a certain period, the complex viscosity abruptly increased, which is the typical viscosity profile during the curing of the toughened epoxy systems [25]. By extending the leveling part and the upraising part of the viscosity-time curve, the obtained intersection is defined as the gelling point of the blends. The time at the gelling point is called a gellation time (t_{gel}). At 110°C, 130°C, and 150°C, the gelation times (t_{gel}) of the blends were approximately 15500s, 6800s, and 2000s, respectively (Table 2). In Figure 4, it is seen
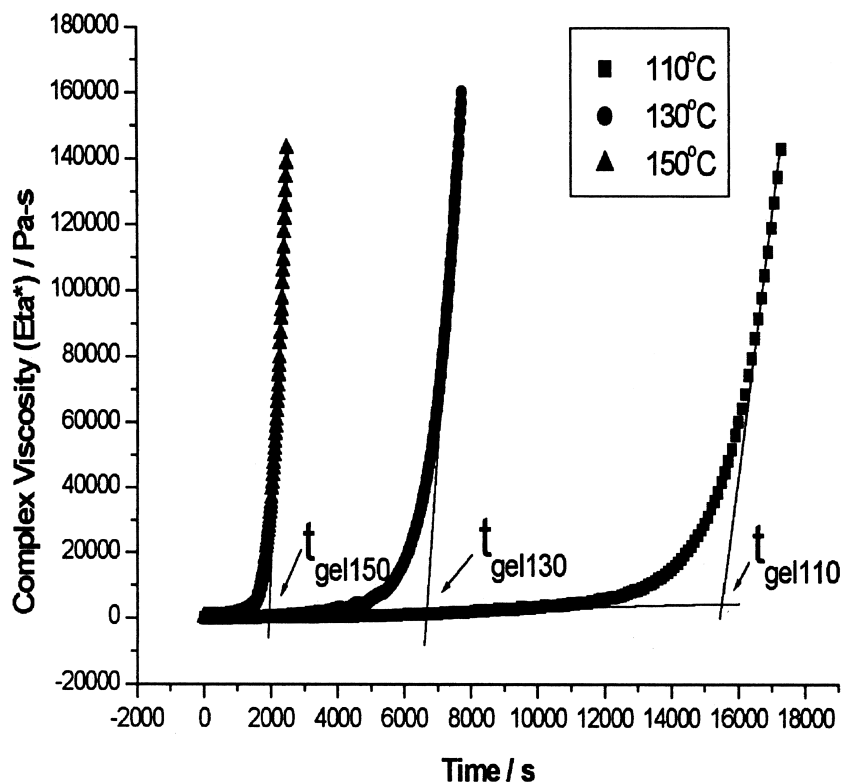

Figure 4. The blend complex viscosity vs. curing time at different temperatures.

that all the gelation times (t_{gel}) of the blends significantly lagged behind the phase structure fixation time (t_{fix}) of the blends. When the phase structure was fixed, the viscosity (v_{fix}) of the blends was about 39, 27, and 36 Pa-s, respectively. Further analysis showed that the viscosity (v_{fix}) of the phase structure fixation was dotted at in a narrow range of approximately 25-40 Pa-s. It was distinct that the development of the interdomain distance had a close relation with the blend viscosity. The curing reaction led less compatibility between PEsI-B and epoxy resin due to the increase of the molecular weight of epoxy resin and drove phase separation to occur. The higher the network density, the larger the driving force for phase separation. However, as the curing reaction proceeded, both the high viscosity of the blend and the low mobility of the components prevented the phase separation from continuing. As discussed above, the phase structures of the blends had been pinned up at a low viscosity stage before the advent of the gelling point. The phase structure was dominated by the system viscosity rather than by the gelling point.
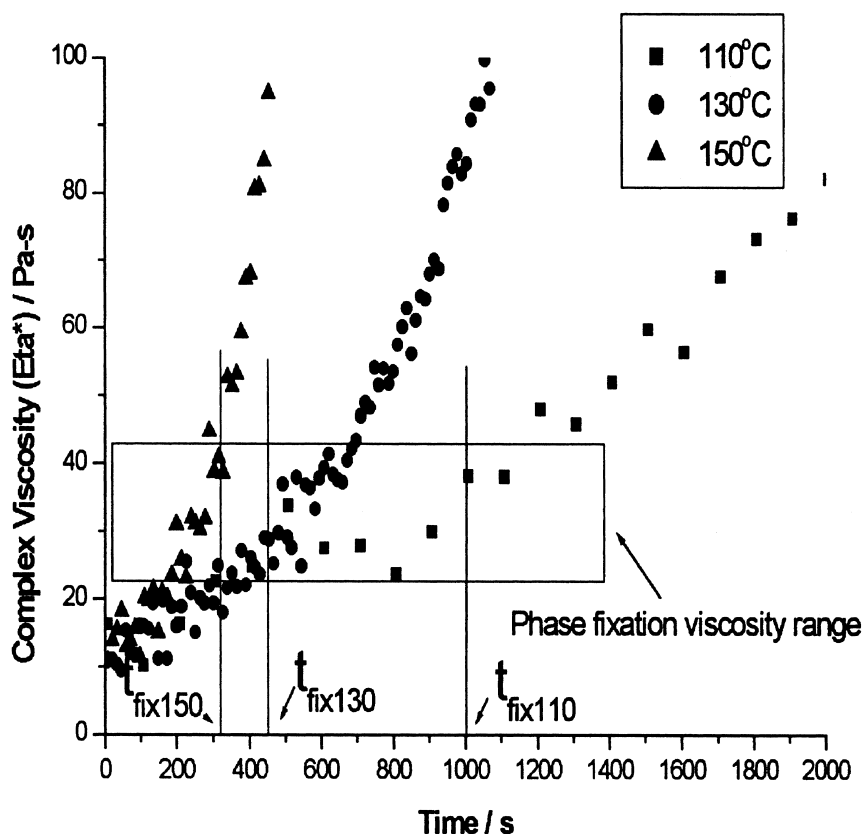

Figure 5. Complex viscosity changes of the blends at the initial stage of curing reaction at different temperatures.

Table 3.   Effect of Pre-curing Temperature on Adhesive Properties

Pre-curing Temperature (°C)	Tensile Lap-Shear Strength (MPa)	Bond Strength (kgf)
110	8.78	63.1
130	4.46	13.4
150	4.21	12.1

Pre-curing stage: 4 hours at pre-curing temperature.
Post-curing stage: 4 hours at 150°C.

Adhesive Property

In the previous study, with the increase of the PEsI-B content from 0 phr to 40 phr in the blend, the tensile lap-shear strength increased 1.23 MPa to 3.28 Mpa and the bond strength from 2.42 kgf to 4.62 kgf. To investigate the effect of the curing temperature on the adhesive properties, the blend with the same composition was pre-cured 4 hours at a different temperature. To eliminate the influence offered by the curing extent, all the samples were post-cured for 10 hours at 150°C. Table 3 shows that the pre-curing temperature had an obvious influence on the adhesive properties of 40 phr PEsI-B modified epoxy blend. The tensile lap-shear strength of the PEsI-B modified epoxy blend increased from 4.21 MPa to 8.78 MPa with the decease of the pre-curing temperature from 150°C to 110°C. In the meanwhile, the bond strength increased from 12.1 kgf to 63.1 kgf. A reasonable explanation is that a low curing temperature had a beneficial effect on the phase separation process. The complete phase separation resulted in a more continuous PEsI-B-in-rich phase structure and a smaller interdomain distance of epoxy-in-rich phase. This result coincided with ones of TRLS, ARES, and SEM.

CONCLUSION

TRLS testing displayed that the phase separation of the blend system followed a spinodial decomposition mechanism at a different curing temperature. Results of TRLS and ARES showed that the phase structure fixation was pinned up by the blend viscosity at the early stage of thecuring reaction, rather than by the gelling point at the late stage of the curing reaction. The increase of the curing temperature accelerated curing reaction and the increase of the blend viscosity prevented phase separation from proceeding. The experiment results suggested that low curing temperature was beneficial to the formation of a shorter interdomain distance of the epoxy-in-rich phase in the blend and to the improvement of the adhesive property of the blend.

ACKNOWLEDGMENT

REFERENCES

1. Yamanaka, K.; Takagi, Y.; Inoue, T. Polymer **1989**, *60*, 1839.
2. Hendrick, L.; Yilgor, I.; Wilkes, G.L.; McGrath, J.E. Polymer. Bull. **1985**, *13*, 201.
3. Bucknall, C.B.; Partridge, I.K. Polymer **1983**, *24*, 639.
4. Raghava, S. J. Polymer. Sci. Part B: Polym. Phys. **1988**, *26*, 65.
5. Kim, B.S.; Chiba, T.; Inoue, T. Polymer **1995**, *36*, 67.
6. Kim, H.Y.; Char, K.H. Ind. Eng. Chem. Res. **2000**, *39*, 955.
7. Cecere, A.; McGrath, J.E. Polymer. Prepr. (Am. Chem. Soc. Div. Polym. Chem.*)*, **1986**, *27*, 299.
8. Bennett, G.S.; Farris, R.J.; Thompson, S.A. Polymer **1991**, *32*, 1637.
9. Bucknall, C.B.; Gibert, A.H. Polymer, **1989**, *30*, 213.
10. Bucknall, C.B.; Gibert, A.H. Polymer **1989**, *30*, 215.
11. Hourston, D.J.; Lane, J.M.; MacBeath, N.A. Polym. International **1991**, *26*, 17.
12. Gilbert, A.H. ; Bucknall, C.B. Makromol. Chem., Macromol. Symp. **1991**, *45*, 289.
13. Hourston, D.J.; Lane, J.M. Polymer **1992**, *33*, 1379.
14. Bonnet, A.; Pascault, J.P.; Sautereau, H. Macromolecules **1999**, *32*, 8524.
15. Park, J.W.; Jim, S.C. Polymers for Advanced Technology, **1996**, *7*, 209.
16. Kim, S.; Chiba, T.; Inoue, T. Polymer **1995**, *36*, 43.
17. Yamanaka, K.; Inoue, T. Polymer **1989**, *30*, 662.
18. Debzi, E.M.; Marchessault, R.H.; Excoffier, G. Macromol. Symp. Aug. **1999**, *143*, 243.
19. Dziedzic, A.; Magierra, A.; Winsiewski, R. Miroelectrion Reliab. Dec. **1998,** *38*, 1893.
20. Luo, Y.; Li, H.; Li, S.J. *Studies on Phase Separation of Polyesterimide-modified Epoxy Resin. I. Effect of Polyesterimide Content on Phase Separation and Adhesive Property*, submitted.
21. Loncrini, D.F. Journal of Polymer Science **1966** *A-1*, 4, 1531.
22. Langsam, M.; Burgoyne, W.F. Journal of Polymer Science: Part A: Polymer Chemistry **1993**, *31*, 909.
23. Seo, Y.; Lee, S.M.; Hong, S.M.; Hwang, S.A.; Hwang, S.S.; Park, T.S.; Kim, K.U. *Polymeric Materials Encyclopedia*, CRC Press: Boca Raton, FL, 1996, 8, 5881.
24. Li, S.J.; Hsu, B.L.;. Harris, F.W.; Cheng, S.Z.D. *The Forth International Symposium on "Toughened Plastic Science and Engineering"*, ACS, San Diego, 1994, p. 27
25. Riew, C.K.; Kinloch, A.J. *Toughened Plastics I*, American Chemical Society, New York, 1992.
26. Girard-Reydet, E.; Sautereau, H.; Pascault, J.P. Polymer **1998**, *39*, 2269.