Polymer 41 (2000) 4451–4459

Improvement of thermal and mechanical properties by control of morphologies in PES-modified epoxy resins

K. Mimura*, H. Ito, H. Fujioka

Mitsubishi El. Co., Advanced Technology R&D Center, 8-1-1, Tsukaguchi-honmachi, Amagasaki City, Hyogo 661-8661, Japan

Received 25 February 1999; received in revised form 28 June 1999; accepted 13 September 1999

Abstract

In order to improve both the heat resistance and the toughness of cured epoxy resins, polyethersulfone (PES) was added to a biphenyl-type epoxy resin. The dispersion state of the PES in the epoxy resin was controlled by changing the molding temperature, and the effect of the morphologies on the heat resistance and toughness of the cured resins was investigated. In the resin with a homogeneous phase morphology, the glass transition temperature (T_g) of the resin containing 10 wt% PES increased about 20°C, and the value of the fracture toughness also increased about 60% more than that of the unmodified resin. This is attributed to the formation of the semi-interpenetrating polymer networks (semi-IPNs) composed of the epoxy network and linear PES. On the resin with phase separation structure, a significant increase in toughness was obtained only when the PES formed a continuous phase morphology. However, higher PES content is required to form the co-continuous phase morphology, which causes the increase in the viscosity of the resin. In addition, the T_g of this system was equal to or only slightly higher than that of the unmodified resin. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Epoxy resin; Polyethersulfone; Toughening

1. Introduction

Epoxy resins have been widely used in the electronics industry because of their superior thermal, mechanical and electrical properties. As applications of epoxy resins spread in advanced technical fields such as printed wiring board and plastic IC packages, high-performance resins have been demanded, that is, mainly the improvement in heat resistance and toughness. In most cases, enhancement of these characteristics is not achieved by only improvement of the structure of epoxy resins. Modifications by elastomers (rubbers) and thermoplastic polymers, therefore, have been investigated.

The modification of epoxy resins with reactive liquid elastomers such as carboxyl-terminated butadiene acrylonitrile rubbers (CTBN) or crosslinked elastomers has been investigated as a successful means of enhancing the fracture toughness of brittle epoxy resins [1–10]. In general, the effective improvement in toughness of elastomer-toughened epoxy resins can be achieved when the elastomer particles are dispersed at the micro level. However, toughness improvements in most elastomer-modified epoxy systems usually result in a significant decrease in the modulus and the glass transition temperature (T_g) of the cured epoxy resins.

More recently, many attempts have been made to modify epoxy resins with a high-performance engineering thermoplastic that has a high T_g and toughness, such as polysulfone (PSF) [11,12], poly(ether sulfone) (PES) [13–16], poly(ether imide) (PEI) [17–19] and polyimide (PI) [20]. The effective improvement in toughness is only obtained 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. But the viscosity of the modified resins drastically increases, which causes the decrease in the handling. In addition, the T_g of the thermoplastic-modified resins is equal to or only slightly higher than that of the unmodified resin because of the formation of the phase-separation morphologies.

On the other hand, attempts have been made to dissolve the thermoplastics in the epoxy resins homogeneously [21–23]. This is a semi-interpenetrating polymer network (semi-IPN) technique which blends two polymers by the entanglement of their networks without chemical bonding between them. The formation of the semi-IPN structure makes it possible to homogeneously blend the epoxy matrix and the thermoplastic or to disperse the thermoplastic in the epoxy matrix microscopically in the combination of

---

* Corresponding author. Tel.: +81-6-6497-7380; fax: +81-6-6497-7463.
E-mail address: mimura@ins.crl.melco.co.jp (K. Mimura).

PII: S0032-3861(99)00700-4

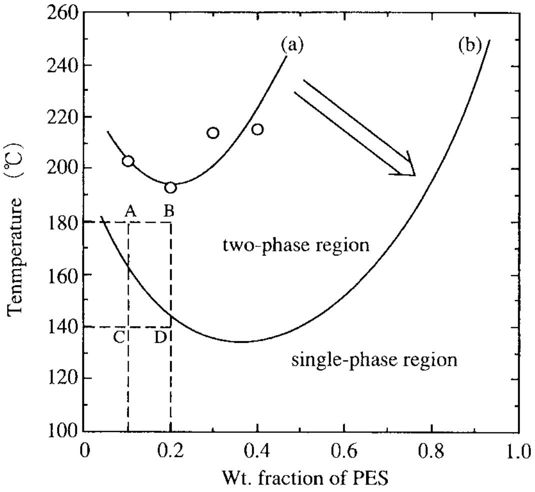


Fig. 1. Phase diagram of epoxy resin/phenol resin/PES mixture. Schematic representation of the variation of phase diagram with curing.

immiscible polymers. We may expect that the blend by the semi-IPN structure has the combined properties of two polymers because of the composite structure at the molecular level. The IPN or semi-IPN technique is one of the effective modifications for epoxy resins with low fractions of the thermoplastic [23].

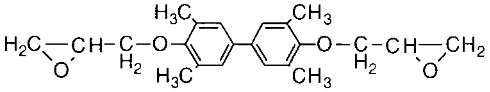
However, little is known about the detailed relationships between the morphology and properties of thermoplastic-modified epoxy polymers, because it is difficult to realize the epoxy resin which has a homogeneous or a phase-separation morphology in an identical thermoplastic-modified system.

This paper, therefore, reports attempts to control the thermoplastic-modified epoxy resins from a homogeneous morphology to a phase-separation one in an identical blend system. Polyethersulfone (PES), the thermoplastic used in this study, is an engineering plastic which has a high heat resistance and toughness. The relationship between the morphology and the thermal-mechanical properties of PES–epoxy blends is discussed. Further, the toughening mechanism was also investigated in detail.

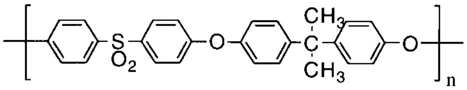
2. Experimental

2.1. Materials and preparation of samples

The epoxy resin used in this work was diglycidyl ether of the biphenyl-type (YX4000; Yuka-Shell Epoxy Co.). Its structure is given below.



The curing agent was phenol novolak type resin (PSM4261; Gunei Chem. Ind. Co.), and the accelerator was triphenylphosphine (TPP). As a modifier, the engineering plastic, polyethersulfone (PES; Teijin Amoko Engineering Plastics) was used. The structure is given below. The concentration of the added PES was varied from 0 to 20% by weight.



The epoxy resin was compounded stoichiometrically with curing agent: one epoxy group corresponds to one hydroxyl group of the curing agent. The compound was stirred at 135°C until the PES dissolved homogeneously in a mixture of the epoxy resin and curing agent. The TPP was then added, and the mixture was rapidly removed from the apparatus. The mixture was molded at 140, 160 or 180°C for 10 min with a transfer press, and then cured at 175°C for 7.5 h.

2.2. Measurements

The phase diagram of epoxy/phenol/PES mixture was obtained with a polymer dynamics analyzer (DYNA-100, Otsuka Electronics Co., Ltd.). The film of the ternary mixture was jumped to each temperature. And the temperature started to phase-separate was plotted as a function of weight fraction of PES (Fig. 1a).

The morphology of fracture surfaces was observed by a scanning electron microscope (SEM: JSM-T20, JEOL, Co. Ltd.). The fracture surfaces were coated with a layer of gold about 200 Å thick.

Dynamic mechanical properties were determined using a non-resonance forced vibration viscoelastometer (RDA, Rheometrics Co., Ltd.). The frequency was adjusted to 1 Hz, and the heating rate was 2°C/min in the atmosphere.

The fracture toughness of the cured epoxy resins was evaluated from the critical value K_c of the stress intensity factor for the initiation of crack growth, which was determined from 3-point bent specimens (6 mm × 15 mm × 75 mm with a span of 60 mm) according to ASTM E399-78. A sharp precrack was formed by carefully tapping a fresh razor blade. The specimen was loaded at a constant cross-head speed (0.5 mm/min). Five specimens were tested for each sample.

The mechanical properties of the cured epoxy resins were determined with a Shimadzu autograph AG-5000D universal testing machine. Flexural tests were carried out at a cross-head speed of 1.5 mm/min according to JIS-K 6911.

The subsurface damage was also examined by a transmission optical microscope (OM: BH-2, Olympus Co., Ltd.). The specimens for OM-observations were prepared with a petrographic polishing technique described by Holic et al. [24]. The thickness of the specimens was less than 35 μm. These sections were inspected with transmitted light with and without crossed polarizers, because Yee [7] demonstrated that the crossed Nicol technique is useful for

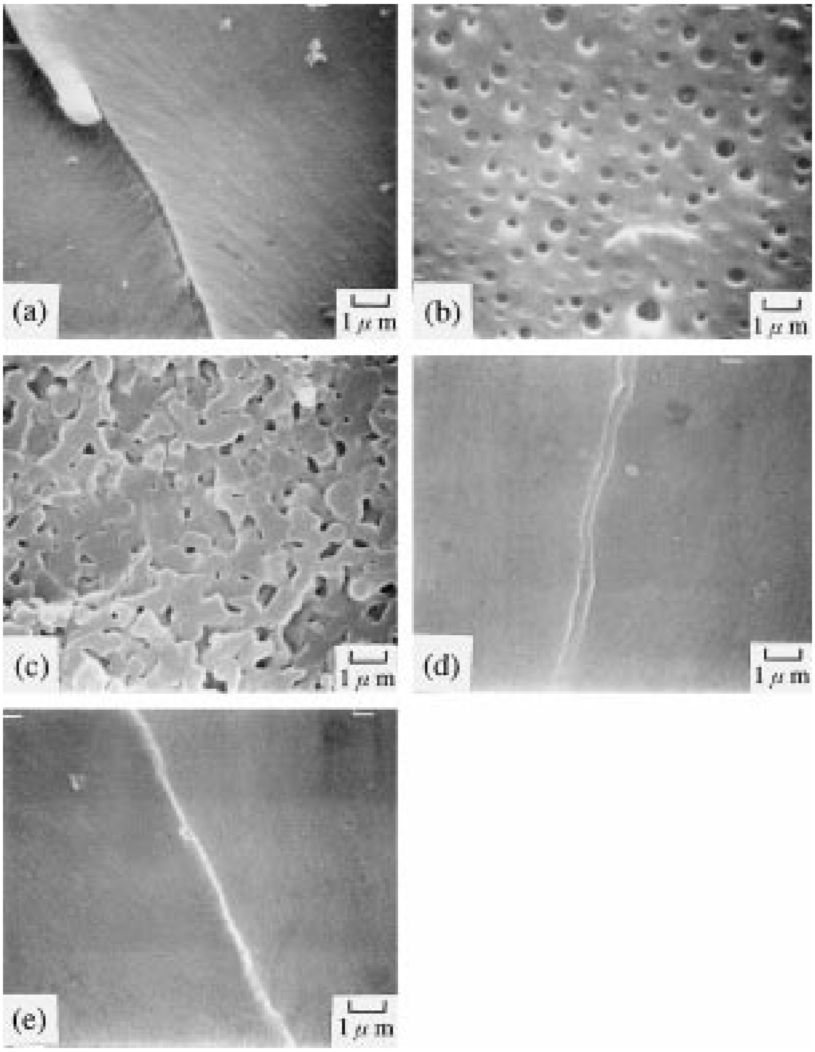


Fig. 2. Scanning electron micrographs of the fractured surfaces for the cured epoxy resins modified with PES: (a) unmodified resin; (b) PES content 10 wt% (180°C); (c) PES content 20 wt% (180°C); (d) PES content 10 wt% (140°C); (e) PES content 20 wt% (140°C).

observing deformations near the crack tip, which induces birefringence.

The ultra-thin section of the modified epoxy resins was examined, using a transmission electron microscope (TEM: JEM-1200EX, JEOL, Co. Ltd.) to observe the microstructure. The specimens for the TEM-observations were stained with ruthenium tetroxide (RuO_4).

3. Results and discussion

3.1. Control of the morphology of cured epoxy resins

It is well known that the mixture of epoxy resin and PES exhibits a lower critical solution temperature (LCST) phase behavior [16], as the phase diagram demonstrates in Fig. 1. As shown in this figure, inclusion of a higher PES content (in the epoxy-rich composition) or a higher curing temperature gives rise to a further progress of the phase separation of PES from the epoxy matrix. However, the morphology is frozen when the T_g exceeds the curing temperature. The final morphology is a result of the competition between the molecular weight increase of the epoxy, leading to phase separation, and the simultaneous crosslinking which suppresses it. Consequently, the control of the morphologies of PES-modified epoxy resins was attempted by changing the molding temperature. In fact, the resin molded at a temperature below 140°C (e.g. point C or D) had a homogeneous morphology, while the resin molded at a temperature above 160°C (e.g. point A or B) had a phase-separated morphology. The morphologies of cured epoxy resins molded at 140 or 180°C, which were observed by scanning electron microscopy (SEM), are shown in Fig. 2. In these pictures, the PES was removed by extracting the samples with THF prior to the SEM examination. It was observed that the epoxy resins molded at 180°C exhibited phase-separation morphologies and that the resins molded at 140°C showed homogeneous phase morphologies. These

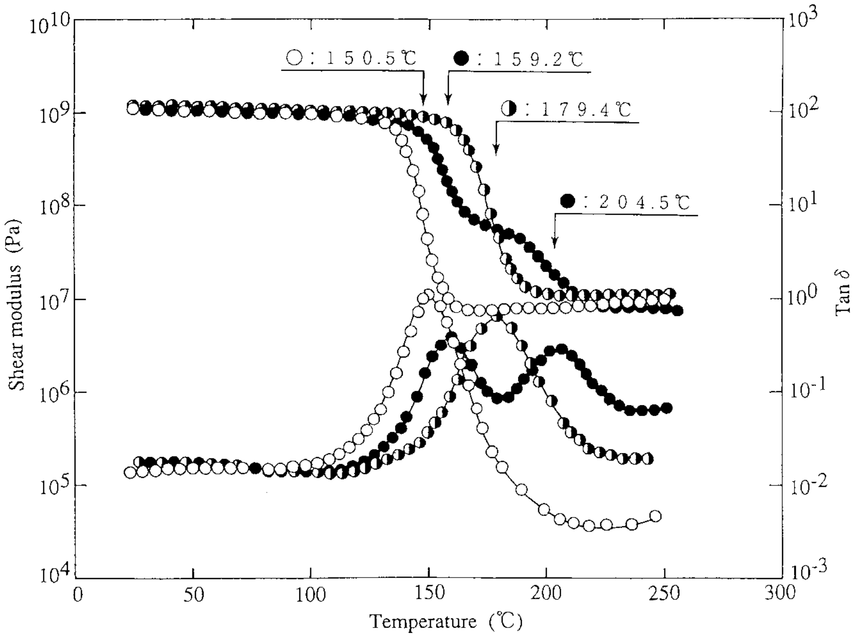


Fig. 3. Dynamic mechanical properties of cured epoxy resins modified with PES (PES content: 20 wt%): ○ unmodified resin; ◑ 140°C cured system; ● 180°C cured system.

results reveal that the change in the molding temperature made it possible to control the phase morphology of the cured resins with constant PES content. On the cured resins molded at 180°C, the morphology significantly depends on PES content. In the cured resin with 10 wt% PES (Fig. 2b), the PES separated from the epoxy matrix and formed a well-defined, dispersed phase whose diameter is about 0.5 μm. When PES content rose to 20 wt% (Fig. 2c), a co-continuous phase morphology composed of the epoxy matrix and PES was observed. It is thought that the drastic change in the morphology in spite of the same molding temperature is attributable to the viscosity of the modified resins. Namely, inclusion of a higher PES content gives rise to an increase in the viscosity of the modified resin, which reduces the rate of phase separation [19–22]. Accordingly, the resin containing 20 wt% PES seems to vitrify with a modulated structure in the early stage of phase separation, because the rate of phase separation is reduced by its high viscosity (Fig. 8). However, in the resin containing 10 wt% PES, the low viscosity makes it possible for PES to separate into individual particles. In contrast, as shown in Fig. 2d and e, the cured epoxy resins molded at 140°C have homogeneous phase morphologies, regardless of PES content. It can be presumed that the resins molded at 140°C will be vitrified before the system is thrust into the two-phase region of the phase diagram.

Dynamic viscoelastic analysis can give information on the microstructure of cured resins. The dynamic mechanical properties of the phase-separated resin and the homogeneous resin are shown in Fig. 3. The unmodified resin showed a single tan δ-peak based on the glass transition temperature (T_g) of the epoxy matrix at 150°C. Two tan δ peaks were observed in the resin molded at high temperature (180°C), which indicates that the resin has a two-phase morphology: one was the peak based on the T_g of the epoxy matrix at 160°C, and the other that of PES at about 205°C. In contrast, the resin molded at 140°C showed a single peak in the middle of the pure epoxy and PES peaks. This result shows that PES in this system was completely dissolved in the epoxy matrix. These results of dynamic mechanical analysis were consistent with the results obtained by SEM observations.

In observing the modulus in the rubbery region, the modulus in the rubbery region of the phase-separation resin was higher than that of the unmodified resin until the T_g of PES. However, the value decreased once the measurement temperature exceeded the T_g of PES. This is attributed to the transfer of PES from the glass state to the molten one. In contrast, the modulus in the rubbery region of the homogeneous resin was equal to or higher than that of the unmodified resin and kept its high value beyond the T_g of PES. The PES used in this study does not have any reactive functional groups with epoxy resins and is not incorporated into the epoxy networks. In the case of modification by non-reactive thermoplastic polymer, the modulus in the rubbery region of the modified resin decreases lower than the values for the unmodified resin, due to a reduction in cross-linking density as a result of the dilution effect of the uncross-linked thermoplastic polymer chains. In these modified-resins with homogeneous morphology, however, the decrease of the modulus in the rubbery region was not observed. Consequently, the high modulus in these resins is attributed to the formation of the semi-interpenetrating polymer networks

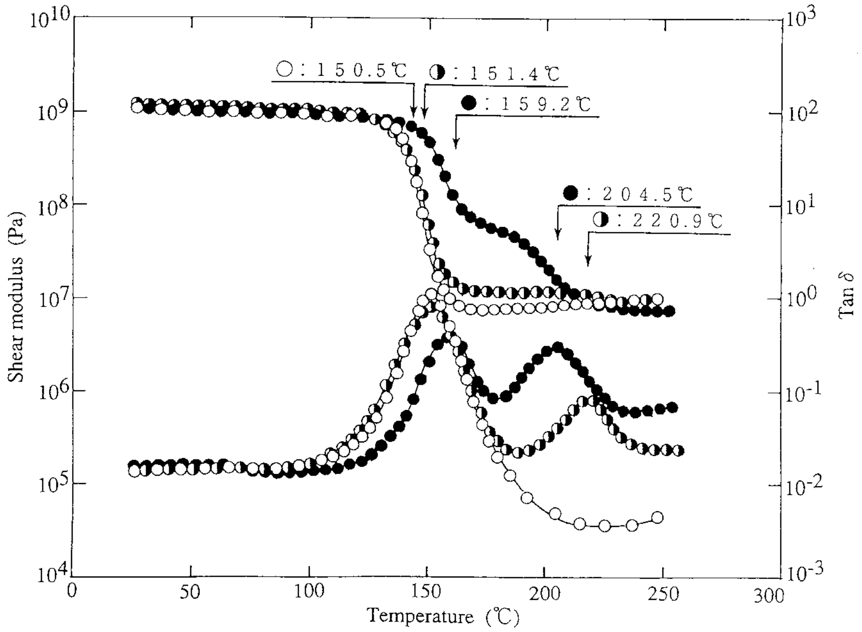


Fig. 4. Dynamic mechanical properties of cured epoxy resins modified with PES; molding temperature—180°C: ○ unmodified resin; ◑ PES content 10 wt%; ● PES content 20 wt%.

(semi-IPNs) composed of the epoxy network and linear PES. The high modulus in the rubbery region can be interpreted as the network interlock of the epoxy matrix and PES.

3.2. Effect of the morphologies of the modified resins on thermal-mechanical properties

In order to investigate the effect of the morphology on the thermal properties, the dynamic mechanical properties of the resins were measured. The dynamic mechanical properties of the resins with phase-separation morphologies, are shown in Fig. 4. The T_g of the unmodified resin was 150°C as previously stated. The T_g of the resin containing 10 wt% PES, which had a particulate morphology, was equal to that of the corresponding unmodified resin. This result indicates that PES phase separated completely from the epoxy matrix.

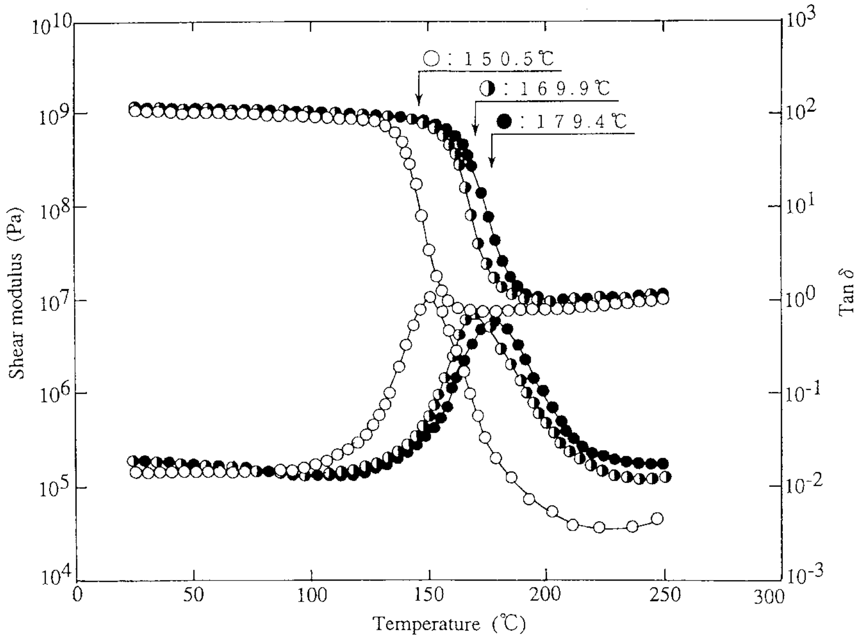


Fig. 5. Dynamic mechanical properties of cured epoxy resins modified with PES; molding temperature—140°C: ○ unmodified resin; ◑ PES content 10 wt%; ● PES content 20 wt%.

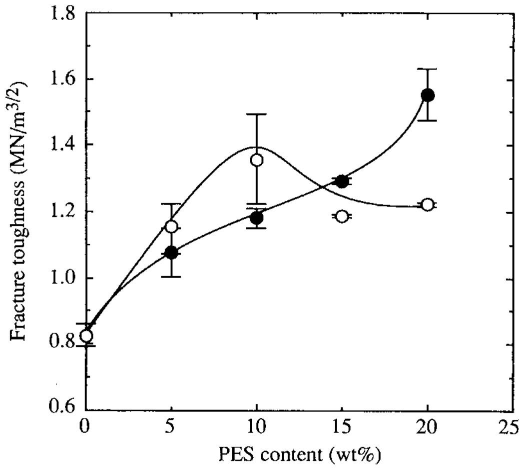


Fig. 6. Plot of fracture toughness vs. modifier contents in cured epoxy resins modified with PES: ○ 140°C cured system; ● 180°C cured system.

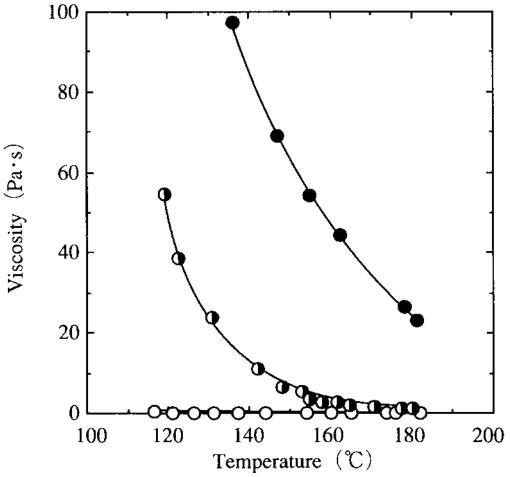


Fig. 8. Viscosity of epoxy resins modified with PES: ○ unmodified resin; ◑ PES content 10 wt%; ● PES content 20 wt%.

And the T_g of the resin containing 20 wt% PES, which had a co-continuous phase morphology, shifted about 10°C higher than that of the unmodified resin. Thus the increases in T_g for the resins with phase-separation morphologies were slight. In opposition to the resins with the phase-separation morphologies, the T_g of the resins with homogeneous phase morphologies shifted towards higher temperature, and the magnitude of the shift increased with an increase in PES content of the blend as shown in Fig. 5. The observed T_g shifts of the modified resin with 10 and 20 wt% PES relative to the unmodified resin were 20 and 30°C, respectively. It is revealed that the system formed the semi-IPN structure shows significant improvement in the T_g of the cured resin with lower PES content compared with the system formed the phase-separation structure.

The effect of morphology on the mechanical properties is next discussed. The fracture toughness of the cured resins modified with PES are shown in Fig. 6. In the resins which formed phase-separation morphologies, the values of the fracture toughness gradually increased with an increase in PES content up to 15 wt%. However, the fracture toughness was drastically increased when 20 wt% PES was added to the mixture. The value of the cured resin containing 20 wt% PES was about 1.9 times greater than that of the unmodified resin. The resin with content below 15 wt% PES formed a particulate morphology, while the resin with 20 wt% PES formed a co-continuous phase morphology. Accordingly, the drastic increase between 15 and 20 wt% PES in toughness is attributed to this transfer of morphology. Thus, for the resin where phase-separation occurred, a significant increase in toughness is achieved only when the thermoplastic forms a continuous phase morphology. In contrast, in the resins with homogeneous phase morphologies, the fracture toughness was greatly improved with lower PES content. With 10 wt% PES, the value of the fracture toughness was about 1.6 times greater than that of the unmodified resin. This result shows that the formation of semi-IPNs structure could improve the fracture toughness of cured resins as well as their heat resistance with lower PES content. However, the fracture toughness in this system decreased at high fractions of PES. This reason will be subsequently discussed.

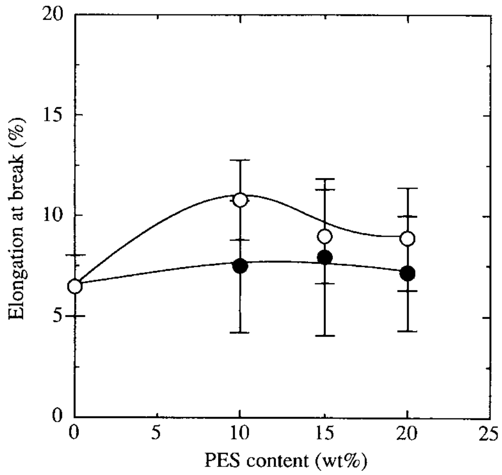


Fig. 7. Plot of elongation vs. modifier contents in cured epoxy resins modified with PES: ○ 140°C cured system; ● 180°C cured system.

Next we measured the flexural properties of the PES-modified resins, and the relationship between the elongation at break and PES content is shown in Fig. 7. Concerning the flexural strength of the modified resins, their values were equal to that of the unmodified resin independent of their morphologies and PES content, but the elongation at break of the modified resins was dependent on them. The elongation at break of the resins with homogeneous phase morphologies remarkably increased at lower fractions of PES, similarly to the behavior of the fracture toughness. The value of the elongation at break in the resin containing 10 wt% PES was about 1.7 times greater than that of the unmodified resin. It can be concluded that the increase in the

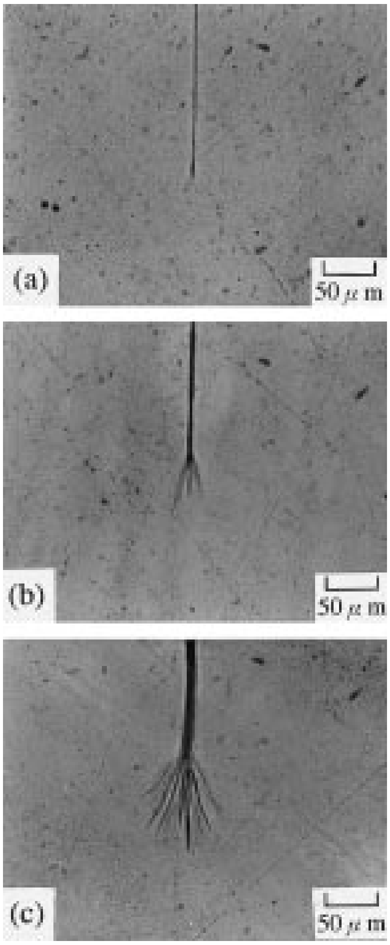


Fig. 9. Optical micrographs of sub-fracture surfaces in PES-modified epoxy resins taken under bright light; molding temperature—180°C: (a) unmodified resin; (b) PES content 10 wt%; (c) PES content 20 wt%.

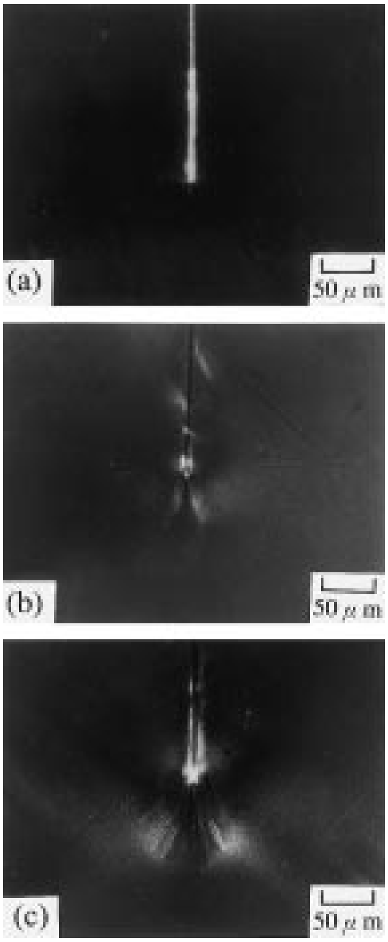


Fig. 10. Optical micrographs of sub-fracture surfaces in PES-modified epoxy resins taken under crossed polarized light; molding temperature—180°C: (a) unmodified resin; (b) PES content 10 wt%; (c) PES content 20 wt%.

fracture toughness is attributed to the increase in the ductility of the modified resin by the formation of the semi-IPN structure. On the other side, the elongation at break of the resins with phase-separation morphologies was equal to that of the unmodified resin, irrespective of their phase-separation state. This suggests that the fracture mechanism of the homogeneous resins forming the semi-IPN structure differs from that of the phase-separation resins which formed the particulate phase or the co-continuous phase.

Fig. 8 shows the temperature dependencies of the viscosity of the epoxy resins modified with PES. The unmodified resin indicates extremely low viscosity regardless of temperature and the value was from 0.015 Pa s at 180°C to 0.05 Pa s at 140°C. For the resin containing 10 wt% PES, the viscosity at 180°C is very low, analogous to the unmodified resin, but its viscosity increased with a decrease in the temperature, and it became very high at 140°C. The viscosity of the resin containing 20 wt% PES was extremely high even when the temperature of the resin was 180°C, and its viscosity at 140°C indicated an enormously high value. Thus, much addition of PES leads to the increase in viscosity of the resin, which causes the decrease in handling.

3.3. Fracture mechanism

To examine the relationship between the phase structure of cured resins and their fracture mechanism, the crack tip region was observed using an optical microscope.

The results of the phase-separated resins with bright light are shown in Fig. 9. In the unmodified resin, it was observed that the pre-crack was extended straightly and that the crack branching did not occur. However, in the 10 wt% PES-modified resin that formed a particulate morphology, the occurrence of crack branching was observed at the crack tip region. In the cured resin modified with 20 wt% PES, which had a co-continuous phase morphology, it was observed that the crack branching spread extensively and reached the region remote from the pre-crack. The results of the same samples observed under crossed polarized light are shown in Fig. 10. In both the particulate phase resin and the co-continuous phase resin, a bright region was scarcely

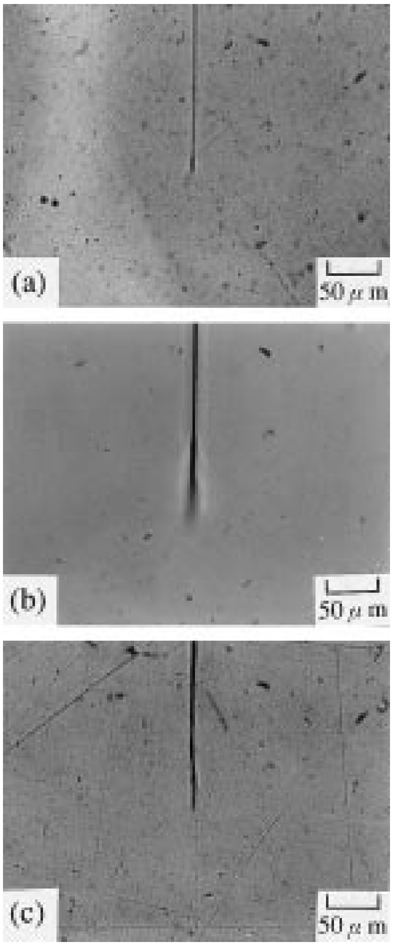


Fig. 11. Optical micrographs of sub-fracture surfaces in PES-modified epoxy resins taken under bright light; molding temperature: 140°C: (a) unmodified resin; (b) PES content 10 wt%; (c) PES content 20 wt%.

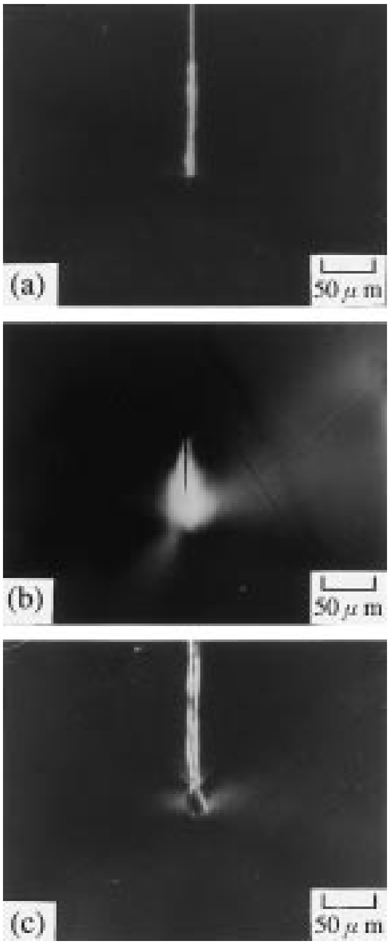


Fig. 12. Optical micrographs of sub-fracture surfaces in PES-modified epoxy resins taken under crossed polarized light; molding temperature: 140°C: (a) unmodified resin; (b) PES content 10 wt%; (c) PES content 20 wt%.

observed. A bright region observed under crossed polarized light represents the region where a shear deformation of the matrix occurred. Consequently, we noticed that there scarcely exists the region where shear deformation occurred in these phase-separated resins.

As previously mentioned, in the phase-separation resins, the progress of the crack is prevented by the dispersed particles of PES, and the crack is split into some branches to avoid progressing through the dispersed particles of PES. Accordingly, it may be concluded that the increase in fracture toughness of the particulate resins is due to the depression of the crack growth with the formation of branches. Moreover, the crack cannot avoid progressing through the tough PES phase once PES forms a continuous phase, which causes the drastic increase in the toughness of the resin with a co-continuous phase morphology.

We next observed the crack tip of the homogeneous phase resins with an optical microscope. From the results observed under bright light (Fig. 11), the crack branching was not observed in any resins, in analogy with the unmodified resin. As shown in Fig. 12, which was observed under crossed polarized light, a very bright region around the crack tip was seen in the resin with 10 wt% PES. Consequently, it was confirmed that in this resin the shear deformation of the matrix occurred, resulting in the drastic improvement in toughness with lower PES content. However, the shear deformation region of the resin with 20 wt% PES was smaller than that of the resin with 10 wt% PES, which leads to the small increase in toughness. Then in order to reveal the reason why the fracture toughness of the modified-resins with the homogeneous morphology decreased at high PES content, these modified-resins were observed in detail with a transmission electron microscope (TEM) and the results are shown in Fig. 13. In these micrographs, the epoxy matrix was stained black by RuO_4 (Fig. 13a). In the observation of the resin containing 10 wt% PES (Fig. 13b), PES formed very fine domains with diameters ranging 50–80 nm in the epoxy matrix. For the resin containing 20 wt% PES (Fig. 13c), it was observed that the obvious PES micro-domains disappeared and that more microscopic PES was dispersed on the whole epoxy matrix. This difference in the microstructure of the resins

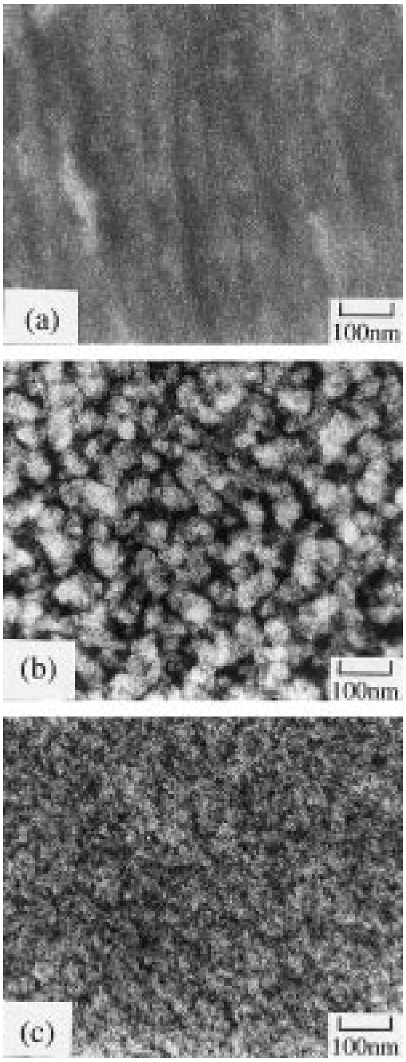


Fig. 13. Transmission electron micrographs of the modified-resins with homogeneous morphology: (a) unmodified resin; (b) PES content 10 wt%; (c) PES content 20 wt%.

with the homogeneous morphology seems to represent as the gap in the toughness. For the resin containing 10 wt% PES, these PES micro-domains seems to be adhered to the epoxy matrix because the PES chains are entangled in the epoxy networks by the formation of semi-IPN structure. It can be concluded, therefore, that the drastic improvement in toughness attributes to the presence of strongly adhering PES micro-domains in the epoxy matrix, which induced the shear deformation of the epoxy matrix. For the resin containing 20 wt% PES, however, these PES micro-domains disappeared. Therefore, the decrease in the improvement effect of the fracture toughness seems to be responsible for the disappearance of the obvious PES micro-domains, which was caused by further inhibition of the phase-separation for the enormously high viscosity of the modified resin.

4. Conclusions

In the blend of PES with epoxy resin, the morphology of the modified epoxy resins influences the thermal–mechanical properties of the cured epoxy resin.

For the resin with a homogeneous morphology, the heat resistance and toughness could be simultaneously improved with lower PES content. It was proved that the semi-IPN structure composed of an epoxy network and linear PES was formed in this system. The increase in T_g is ascribed to the entanglement in the network of the epoxy matrix and PES. In the resin with lower PES content, a presence of PES micro-domains with diameters ranging 50–80 nm was observed in the epoxy matrix. It is considered, therefore, that the increase in the fracture toughness is due to the domain-induced shear deformation of the epoxy matrix. But in the resin with higher PES content, the disappearance of the obvious PES micro-domains by further inhibition of the phase-separation was observed, which leads to the decrease in the improvement effect of the fracture toughness.

However, for the resin where phase separation occurred, a great increase in toughness was obtained only when the PES formed a continuous phase morphology. A higher PES content is needed to form the continuous phase morphology, which causes the increase in the viscosity of the resin. In addition, the T_g of the thermoplastic-modified resins is equal to or only slightly higher than that of the unmodified resin.

References

[1] Rowe EH, Seibert AR, Drake RS. Mod Plast 1970;47:110.
[2] Bascom WD, Cottington RL, Jones RL, Peyser PJ. J Appl Polym Sci 1975;19:2545.
[3] Kinloch AJ, Shaw SJ, Hunston DL. Polymer 1983;24:1355.
[4] Kinloch AJ, Hunston DL. J Mater Sci Lett 1987;6:137.
[5] Yee AF, Pearson RA. J Mater Sci 1986;21:2462.
[6] Pearson RA, Yee AF. J Mater Sci 1986;21:2475.
[7] Pearson RA, Yee AF. J Mater Sci 1991;26:3828.
[8] Huang Y, Kinloch AJ. J Mater Sci 1992;27:2763.
[9] Yamanaka K, Inoue T. J Mater Sci 1990;25:241.
[10] Kunz SC, Sayre JA, Assink RA. Polymer 1982;23:1897.
[11] Hedrick JL, Yilgor I, Wilkes GL, McGrath JE. Polym Bull 1985;13:201.
[12] Min B-G, Hodgkin JH, Stachurski ZH. Polym Bull 1993;50:1511.
[13] Kubotera K, Yee AF. ANTEC'92 1992:2610.
[14] Hedrick JL, Yilgor I, Jurek M, Hedrick JC, Wilkes GL, McGrath JE. Polymer 1991;32:2020.
[15] Yoon TH, Liptak SC, Priddy D, McGrath JE. ANTEC'93 1993:3011.
[16] Yamanaka K, Inoue T. Polymer 1989;30:662.
[17] Bucknall CB, Gilbert AH. Polymer 1989;30:213.
[18] Hourston DJ, Lane JM. Polymer 1992;33:1379.
[19] Cho JB, Hwang JW, Cho K, An JH, Park CE. Polymer 1993;34:4832.
[20] Biolley N, Pascal T, Sillion B. Polymer 1994;35:558.
[21] Nishi S, Sasaki S, Hasuda Y. ACS Polym Prep 1987;28(2):175.
[22] Teng K-C, Chang F-C. Polymer 1996;37:2385.
[23] Tanaka N, Iijima T, Fukuda W, Tomoi M. Polym Int 1997;42:95.
[24] Holic AS, Kambour RP, Hobbs SY, Fink DG. Microstruct Sci 1979;7:357.