

Effects of morphology on toughening of tetrafunctional epoxy resins with poly(ether imide)

J. B. Cho, J. W. Hwang, K. Cho, J. H. An and C. E. Park*

Department of Chemical Engineering, Pohang Institute of Science and Technology, and Organic Materials Division, Research Institute of Industrial Science and Technology, PO Box 125, Pohang 790-600, Korea

(Received 27 October 1992; revised 5 April 1993)

Tetraglycidyl-4,4'-diaminodiphenyl methane based resin with 30 phr diaminodiphenyl sulfone as curing agent was toughened with poly(ether imide) (PEI). The effects of morphology on the fracture toughness of modified epoxy resins were investigated. Morphology was controlled by changing the curing conditions. The co-continuous structure and morphology of the PEI spherical domain dispersed in the epoxy matrix were obtained. Phase-inversed morphology with PEI matrix was also obtained with 30 phr PEI content. The cured resin with phase-inversed morphology showed the highest fracture toughness. The modified epoxy resins with enhanced fracture toughness exhibited other improved mechanical properties such as flexural strength, flexural modulus and strain at break.

(Keywords: tetrafunctional epoxy resin; poly(ether imide); morphology)

INTRODUCTION

Multifunctional epoxy resins have been used for many important applications such as adhesives, semiconductor encapsulants, and matrix resins for advanced fibre composites due to their high thermal resistance, high tensile strength and modulus, and good chemical resistance. However, further growth of these highly crosslinked materials is limited because of their inherent brittleness. To overcome this drawback many researchers have studied rubber toughening. However, they^{1,2} had limited success because the energy dissipation mechanisms for highly crosslinked thermoset resins are cavitation in the rubber particle, shear band near the crack tip, and rubber-bridging rather than crazing and shear yielding observed in rubber-toughened thermoplastics.

Generally, it is widely recognized that rubber toughening or hard filler modification cannot induce massive yielding with highly crosslinked matrices. Recently, toughening of highly crosslinked resins was explored by physical blending with high performance engineering thermoplastics such as poly(ether sulfone) (PES)^{3,4}, polysulfone (PSF)⁵, poly(ether ketone) (PEK)⁶ and poly(ether imide) (PEI)⁷. The improvement in fracture toughness by making polymer alloys of thermosets with thermoplastics is achieved without the expense of modulus.

Yamanaka and Inoue⁸ studied the structure development in epoxy resins modified with PES. They showed that the morphology in a multicomponent thermosetting resin can be controlled by the content of thermoplastics and

the curing conditions leading to competition between phase separation and the crosslink reaction. Kubotera and Yee³ also mentioned the importance of morphology on the fracture toughness of PES-modified epoxy resins.

This paper will show the effects of morphology on the toughening of PEI-modified tetrafunctional epoxy resins and how to control the morphology. To maximize fracture toughness, toughening mechanisms are also explored.

EXPERIMENTAL

Materials

The epoxy resin used was Ciba-Geigy MY720 resin, which is tetraglycidyl-4,4'-diaminodiphenyl methane (TGDDM). The resin was cured with 30 phr of diaminodiphenyl sulfone (DDS) manufactured by Ciba-Geigy. General Electric's Ultem 1000 PEI was used as a toughening agent.

Sample preparation

Modified epoxy resins containing 10–30 phr PEI were prepared by the following procedure: PEI was dissolved in methylene chloride (CH_2Cl_2) and mixed with TGDDM at room temperature. The solution was heated in an oil bath for 2 h to 135°C to drive off most of the CH_2Cl_2 , and residual solvent was removed under vacuum at 135°C for 1 h. The DDS hardener was then added with vigorous stirring for about 5 min. After eliminating air bubbles under vacuum for 30 min, the resin was poured into a Teflon-coated aluminium plate mould, and cured in the oven.

Pellets of the neat PEI were compression-moulded at 270°C and 10 MPa.

* To whom correspondence should be addressed

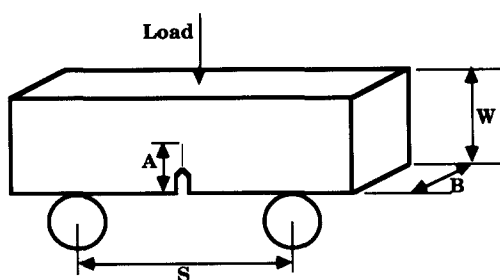


Figure 1 Schematic diagram of the parameters required to calculate the fracture toughness (see text)

In order to control the morphology three different curing conditions were used: (A) 140°C for 2 h and 190°C for 2 h; (B) 70°C for 88 h, 140°C for 2 h and 190°C for 2 h; (C) 190°C for 4 h.

Mechanical properties and morphology

Fracture toughness, K_{IC} , was measured by the notched three-point bending test with a crosshead speed of 1.3 mm min⁻¹ according to ASTM E399. Fracture toughness was calculated using the following equation:

$$K_{IC} = \frac{P_c S}{BW^{3/2}} f\left(\frac{A}{W}\right) \quad (1)$$

where

$$f\left(\frac{A}{W}\right) = 3\left(\frac{A}{W}\right)^{1/2} \frac{\left[1.99 - \left(\frac{A}{W}\right)\left(1 - \frac{A}{W}\right)\left(2.15 - 3.93\frac{A}{W} + 2.7\frac{A^2}{W^2}\right)\right]}{\left[2\left(1 + 2\frac{A}{W}\right)\left(1 - \frac{A}{W}\right)^{3/2}\right]}$$

and P_c is the load at crack initiation, B is the thickness of the specimen (3 mm), S is the span width (24 mm), W is the width of the specimen (6 mm) and A is the crack length (3 ± 0.3 mm) (Figure 1).

Central V-notches were machined in the bars and extended by pressing a fresh razor blade into the tip of the notch to give a crack length of 3 ± 0.3 mm. Flexural properties were measured by the three-point bending test with a crosshead speed of 1.28 mm min⁻¹ according to ASTM D790. The dimensions of the specimens were 57 × 12 × 3 mm with a span of 48 mm.

Fracture surfaces were examined by a scanning electron microscope to investigate the morphology of the modified epoxy resins.

RESULTS AND DISCUSSION

When the PEI content was <20 phr, the standard morphology of the modified epoxy resins was spherical inclusion of PEI dispersed in the epoxy matrix, which can be obtained by curing the resin mixture with curing condition A (140°C for 2 h and 190°C for 2 h). Yamanaka and Inoue⁸ have already presented the phase separation scheme of thermoplastics-modified epoxy resin, where the homogeneous mixture starts to phase separate by spinodal decomposition after the temperature jump to the curing temperature, resulting in the development of a co-continuous structure in the early stage, as schematically shown in Figure 2⁹. As the reaction

proceeds, spherical domains are formed as a result of the coarsening process. The progress of the phase separation is limited either by high viscosity or by the lack of mobility caused by continuing polymerization and the crosslink reaction. Thus, the final morphology is determined by the balance of two competing processes, phase separation and polymerization. In this study, co-continuous structure is obtained by curing the resin mixture with curing condition B (70°C for 88 h, 140°C for 2 h and 190°C for 2 h). By curing at low temperature for a long time, the resin mixture is gelled in the early stage of phase separation which results in co-continuous structures as shown in Figure 2a.

The effect of morphology on fracture toughness of PEI-modified epoxy resins is shown in Table 1. The resin with co-continuous structure shows better fracture toughness than that with a morphology of PEI spherical domain throughout the PEI content from 10 to 20 phr. A greater increase in fracture toughness is observed the higher the PEI content. Figure 3 shows scanning electron micrographs of PEI-modified epoxy resins with two different morphologies. In co-continuous structure, the toughening mechanism seems to be the result of the yielding of PEI, and more yielding is seen the higher the PEI content. The average particle size of the PEI domain increased from 0.7 to 1.3 μm with increasing PEI content.

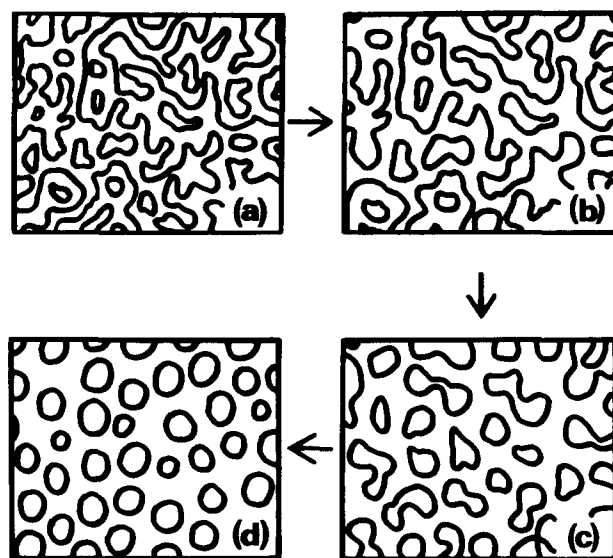


Figure 2 Schematic diagram of phase separation: (a) co-continuous structure; (b) similar structure with longer periodic distance; (c) disconnected structure; (d) spherical domain structure. Reproduced from reference 9

Table 1 Effect of morphology on fracture toughness (in MPa m^{1/2}) of PEI-modified epoxy resin^a

Curing condition	PEI content (phr)			
	0	10	15	20
140°C, 2 h 190°C, 2 h (Spherical particles of PEI)	0.51 ± 0.03	0.68 ± 0.03	0.76 ± 0.03	0.81 ± 0.04
70°C, 88 h 140°C, 2 h 190°C, 2 h (Co-continuous structure)	0.51 ± 0.03	0.76 ± 0.04	0.87 ± 0.05	1.02 ± 0.06

^a Fracture toughness of PEI is 3.61 ± 0.17 MPa m^{1/2}

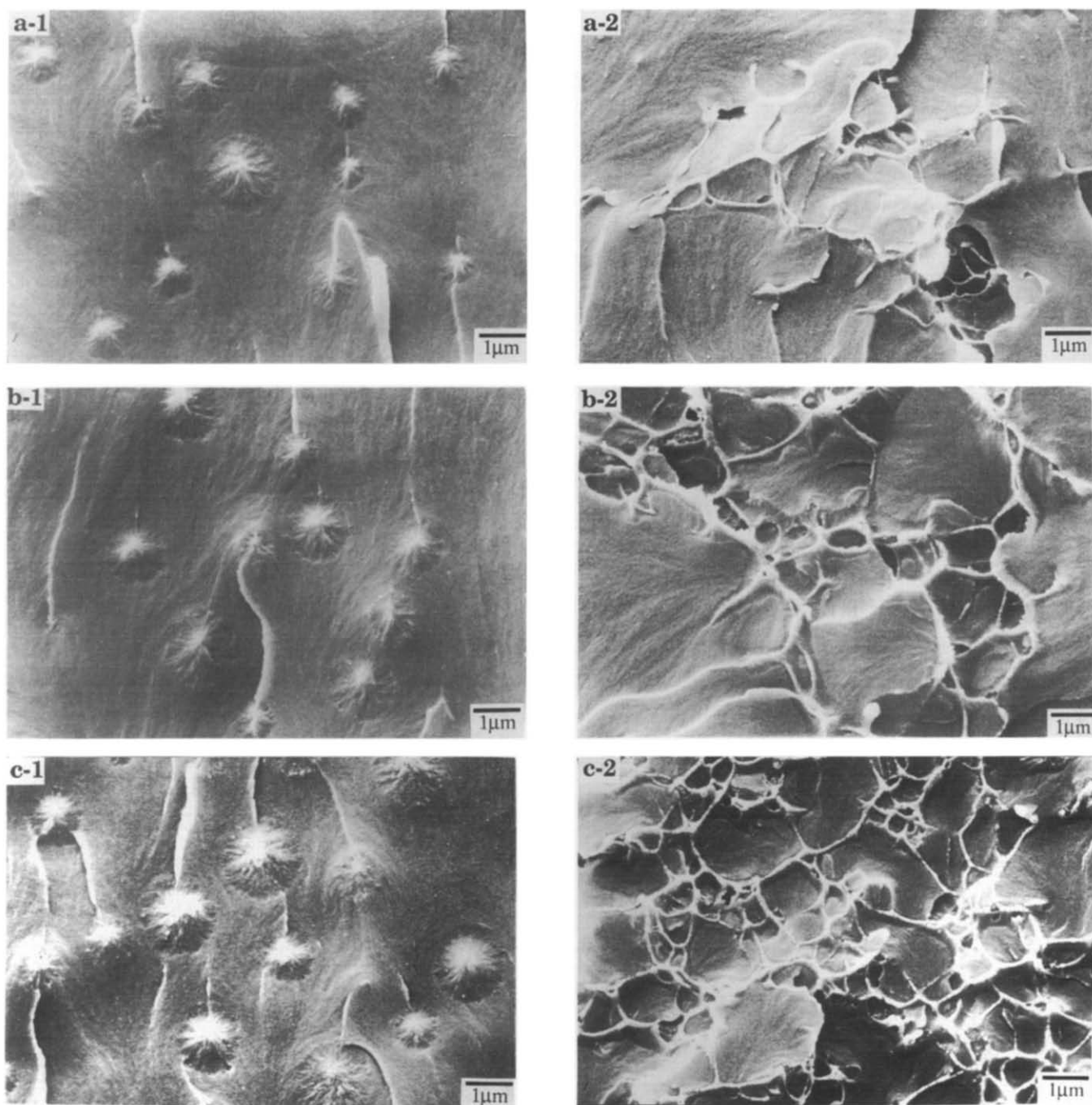


Figure 3 Scanning electron micrographs of PEI-modified epoxy resins with two different morphologies: (1) PEI spherical domain; (2) co-continuous structure. PEI content (phr): (a) 10; (b) 15; (c) 20

Table 2 Effects of morphology on flexural properties of PEI-modified epoxy resin

Morphology	PEI content (phr)	Flexural modulus (MPa)	Flexural strength (MPa)	Strain at break (%)
Neat epoxy resin	0	3388 ± 5	172.3 ± 14.2	5.50 ± 0.56
Neat PEI		3126 ± 63	184.6 ± 4.7	7.99 ± 0.32 ^a
Spherical particle	10	3533 ± 69	143.8 ± 33.2	4.50 ± 0.13
	15	3342 ± 69	173.7 ± 18.7	5.80 ± 0.96
	20	3716 ± 10	179.1 ± 6.3	5.86 ± 0.10
Co-continuous structure	10	3619 ± 105	178.6 ± 16.9	5.50 ± 0.60
	15	3655 ± 71	200.0 ± 12.2	6.60 ± 0.70
	20	3457 ± 30	207.3 ± 8.3	7.16 ± 0.70

^a Strain at yield

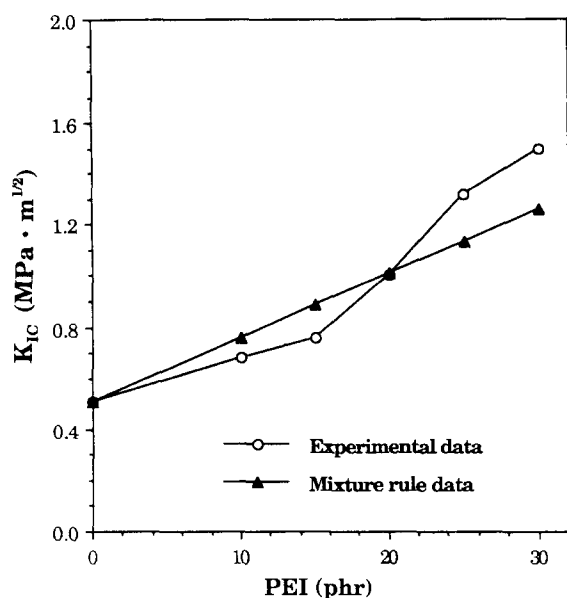


Figure 4 Effect of PEI content on fracture toughness of PEI-modified epoxy resin cured with curing condition A

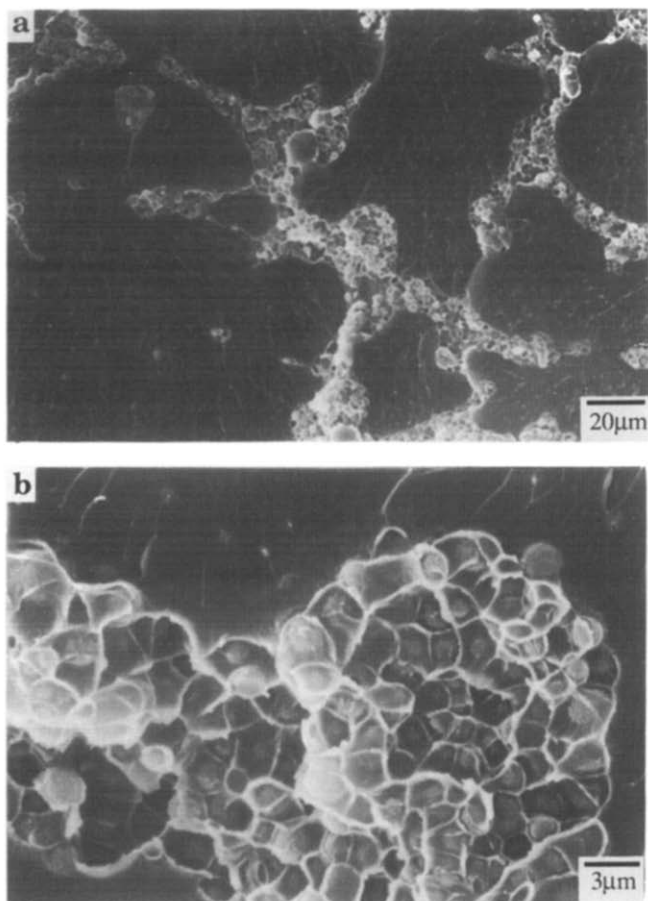


Figure 5 Combined morphology of phase-inversed structure and PEI spherical domain. (b) is a higher magnification view of (a)

Table 2 shows the effects of morphology on flexural properties of PEI-modified epoxy resins. Since the mechanical properties of PEI are better than those of neat epoxy resin, mechanical properties such as flexural modulus, flexural strength and strain at break are improved by incorporating PEI as a toughening agent,

and the improvements are more pronounced with a morphology of co-continuous structure especially in flexural strength and strain at break.

The fracture toughness of PEI-modified epoxy resins steeply increases with > 20 phr PEI content and is higher than that of the arithmetic mean value as shown in Figure 4. When the PEI content exceeds 20 phr, phase inversion appears to start and results in a combined morphology of phase-inversed structure and PEI spherical domain (Figure 5), which causes a sharp increase in fracture toughness of PEI-modified epoxy resins. With 30 phr PEI content complete phase inversion is shown with the epoxy spherical domain dispersed in the PEI matrix. In the phase-inversed structure, the epoxy particle size can be controlled by changing the curing conditions as shown in Table 3 and Figure 6. A larger

Table 3 Effect of epoxy particle size on fracture toughness of PEI-modified epoxy resins with phase-inverted structure

Curing condition	PEI content (phr)	Morphology	Fracture toughness (MPa m ^{1/2})
140°C, 2 h	30	Spherical particle 3–4 μm	1.42 ± 0.05
190°C, 2 h			
70°C, 88 h	30	Non-spherical particle 0.5–1 μm	1.01 ± 0.04
140°C, 2 h			
190°C, 2 h	30	Spherical particle 8–10 μm	1.60 ± 0.04
190°C, 4 h			

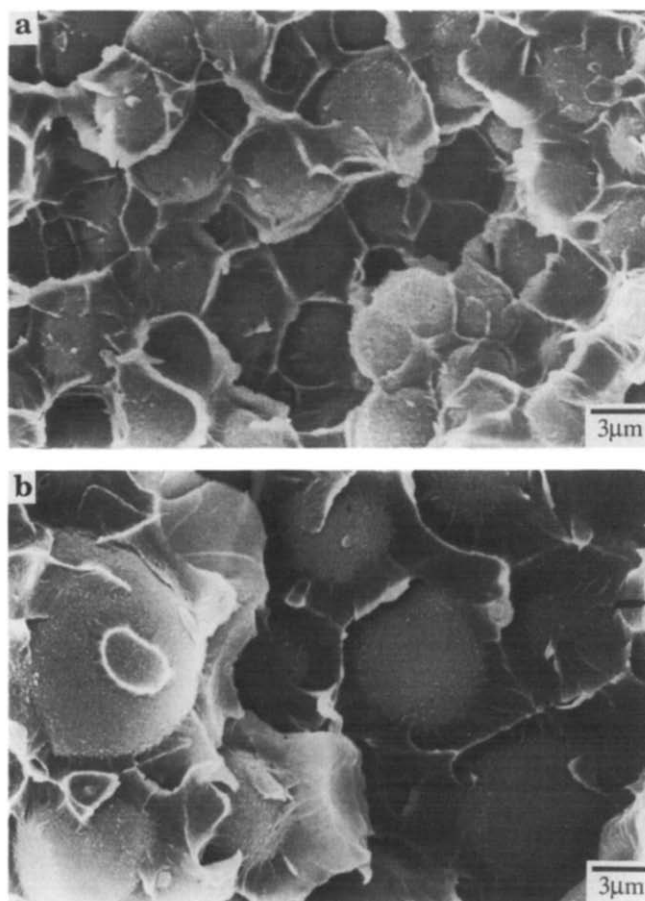
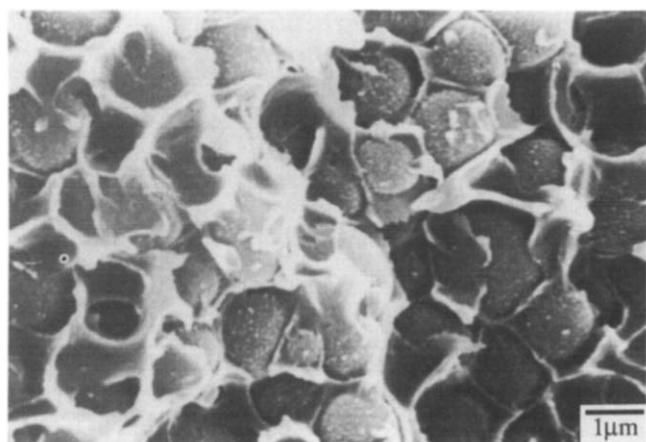


Figure 6 Scanning electron micrographs of 30 phr PEI-modified epoxy resins with different curing conditions: (a) 140°C for 2 h and 190°C for 2 h; (b) 190°C for 4 h

Table 4 Flexural properties of PEI-modified epoxy resins with phase-inversed structure

Curing condition	PEI content (phr)	Flexural modulus (MPa)	Flexural strength (MPa)	Strain at break (%)
140°C, 2 h 190°C, 2 h	30	3113 ± 329	226.4 ± 52.7	6.05 ± 0.70
70°C, 88 h 140°C, 2 h 190°C, 2 h	30	3346 ± 107	167.1 ± 11.2	5.36 ± 0.61
190°C, 4 h	30	3517 ± 102	189.0 ± 6.8	5.90 ± 0.39

**Figure 7** Scanning electron micrograph of 50 phr PEI-modified epoxy resins cured with curing condition A

particle size is obtained with a higher curing temperature since the rate of phase separation is increased due to enhanced chain mobility, while the rate of crosslink reaction is not increased that much. Smaller particle size is obtained by increasing the PEI content from 30 to 50 phr as shown in *Figure 7*. Higher PEI content seems to increase the viscosity of the resin mixture, which reduces the rate of phase separation. The above results are consistent with those of Yamanaka and Inoue⁸. The fracture toughness is improved by increasing the average epoxy particle size, making the distance between the epoxy particles longer. It seems that fracture toughness is sharply increased since the crack goes through the PEI matrix in the phase-inversed structure, and a crack path through the PEI matrix is more plausible with a longer distance between epoxy particles. Consequently, maximum ductile yielding of PEI can be achieved by making a crack path go through a PEI matrix with a phase-inversed structure. Flexural properties of a phase-inversed structure are shown in *Table 4*. Only a dramatic increase in fracture toughness occurs; there are no dramatic improvements in the other mechanical properties.

Since the toughening mechanism of PEI-modified epoxy resins is the ductile yielding of PEI, a co-continuous morphology with <20 phr PEI content and larger epoxy

particle size in a phase-inversed structure with >30 phr PEI content are required to obtain maximum yielding of PEI.

CONCLUSIONS

In the toughening of tetrafunctional epoxy resin with PEI, the morphology of the modified epoxy resins is very important. With <20 phr PEI content, a co-continuous structure yields better fracture toughness than the morphology of a PEI spherical domain dispersed in the epoxy matrix since more ductile yielding of PEI is shown in a co-continuous structure.

Phase inversion starts with >20 phr PEI content, and complete phase inversion is shown with 30 phr PEI content. The fracture toughness of a phase-inversed structure with epoxy spherical domain is better than that of a co-continuous structure, and can be further improved by increasing the epoxy particle size and widening the distance between epoxy particles, making the crack path through the PEI matrix more plausible.

The morphology of a thermoset/thermoplastic alloy can be controlled by changing the curing conditions. Co-continuous structure can be obtained by fixing the morphology of the early stage of phase separation. In the phase-inversed structure, the epoxy particle size can be increased with a higher curing temperature, promoting phase separation.

ACKNOWLEDGEMENT

This paper was supported by the Korea Science and Engineering Foundation (project number 90-04-00-09).

REFERENCES

- 1 Pearson, R. A. and Yee, A. F. *J. Mater. Sci.* 1991, **26**, 3828
- 2 Huang, Y. and Kinloch, A. J. *J. Mater. Sci.* 1992, **27**, 2763
- 3 Kubotera, K. and Yee, A. F. *ANTEC* 1992, 2610
- 4 Hedrick, J. L., Yilgor, I., Jurek, M., Hedrick, J. C., Wilkes, G. L. and McGrath, J. E. *Polymer* 1991, **32**, 2020
- 5 Hedrick, J. L., Yilgor, I., Wilkes, G. L. and McGrath, J. E. *Polym. Bull.* 1985, **13**, 201
- 6 Iijima, T., Tochimoto, T. and Tomoi, M. *J. Appl. Polym. Sci.* 1991, **43**, 1685
- 7 Bucknall, C. B. and Gilbert, A. H. *Polymer* 1989, **30**, 213
- 8 Yamanaka, K. and Inoue, T. *Polymer* 1989, **30**, 662
- 9 Yamanaka, K., Takagi, Y. and Inoue, T. *Polymer* 1989, **30**, 1839