

Toughening of Cycloaliphatic Epoxy Resins by Poly(ethylene phthalate) and Related Copolyesters

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ABSTRACT: Poly(ethylene phthalate) (PEP) and poly(ethylene phthalate-co-ethylene terephthalate) were used to improve the brittleness of the cycloaliphatic epoxy resin 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexane carboxylate (Celoxide 2021™), cured with methyl hexahydrophthalic anhydride. The aromatic polyesters used were soluble in the epoxy resin without solvents and effective as modifiers for toughening the cured epoxy resin. For example, the inclusion of 20 wt % PEP (MW, 7400) led to a 130% increase in the fracture toughness (K_{IC}) of the cured resin with no loss of mechanical and thermal properties. The toughening mechanism is discussed in terms of the morphological and dynamic viscoelastic behaviors of the modified epoxy resin system. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 84: 388–399, 2002; DOI 10.1002/app.10363

Key words: cycloaliphatic epoxy resins; methyl hexahydrophthalic anhydride; poly(ethylene phthalate); modification; fracture toughness; morphology

INTRODUCTION

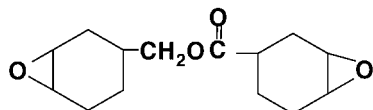
Epoxy resins are among the most important high-performance thermosetting polymers and have wide use as structural adhesives and matrix resin for fiber composites, but their cured resins have one drawback; they are brittle and have poor resistance to crack propagation. The toughness of epoxy resins has been increased by blending them with reactive liquid rubbers such as carboxyl-terminated butadiene acrylonitrile rubbers (CTBN)¹ or terminally functionalized engineering thermoplastics.^{2,3} Engineering thermoplastics are interesting materials to use as modifiers for epoxy resins from the viewpoint that they maintain the mechanical and thermal properties of the matrix resins, in contrast to the reactive elastomers. Modification of epoxy resins with various types of

ductile thermoplastics as alternatives to the reactive rubbers for improving the toughness of epoxy resins has been studied. Various kinds of engineering thermoplastics have been examined as modifiers, and commercial poly(ether sulfone)s,^{4–6} functionalized polysulfones,^{2,7–10} poly(etherimide)s^{3,11–14} poly(aryl ether ketone)s,^{15–17} poly(phenylene oxide),¹⁸ and poly(butylene terephthalate)¹⁹ have been reported to be effective modifiers. *N*-Phenylmaleimide–styrene copolymers, *N*-phenylmaleimide–*N*-cyclohexylmaleimide–styrene terpolymers, and related copolymers were also reported to be effective modifiers for the diglycidyl ether of bisphenol-A (DGEBA).^{20–24}

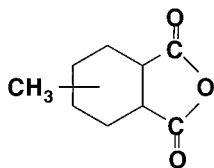
In a previous paper²⁵ we reported that aromatic polyesters, prepared by the reaction of phthalic acids and α, ω -alkanediols, were effective modifiers for more lightly cross-linked DGEBA resin cured with methyl hexahydrophthalic anhydride. The highly cross-linked epoxy resins are used as the matrices of advanced composites. Poly(ethylene phthalate) (PEP), poly(butylene

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**3,4-Epoxyhexylmethyl
3,4-epoxycyclohexane carboxylate
(Celoxide 2021™)**



Methyl hexahydrophthalic anhydride

Scheme 1

phthalate) (PBP), and related copolyesters have been reported as effective modifiers for highly cross-linked epoxy resins.^{26,27} In the modification of epoxy resins with PEP or PBP, the toughening was achieved with no loss of mechanical properties because of particulate structures of the modified resins.

Cycloaliphatic epoxy resins have high heat deflection temperatures and good high-temperature electrical properties.²⁸ However, there are no reports on the modification of cycloaliphatic epoxy resins by thermoplastics: CTBN²⁹ and silicone elastomers³⁰ were used as modifiers. This paper reports the modification of acid anhydride-cured cycloaliphatic epoxy resin by PEP and poly(ethylene phthalate-co-ethylene terephthalate) (terephthalate unit 50 mol%; PEPT). The effect of structure, molecular weight (MW), and amount of the polyesters used on the toughness of the cured resin was examined.

EXPERIMENTAL

Materials

The cycloaliphatic epoxy resin was a low viscous 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexane carboxylate (Celoxide 2021™; Daicel Chemical Industrial Corp.; Scheme 1). Methyl hexahydrophthalic anhydride (MHHPA; Epiclone B-650; Dainippon Ink and Chemical Inc.) was used as a curing agent. PEP and PEPT were prepared by the reaction of 1,2-ethanediol and aromatic dicarboxylic acid (phthalic anhydride and terephthalic

acid) as reported previously.²⁰ Other reagents were used as received.

Measurements

Infrared (IR) spectra were measured with a Fourier transform infrared (FTIR) spectrophotometer (Shimadzu 4000 type, Kyoto, Japan). Proton nuclear magnetic resonance (¹H NMR) spectra were recorded on a 90 MHz instrument (JEOL JNM-9MX 90, Tokyo, Japan), using CDCl₃ as solvent and tetramethylsilane as internal standard. Molecular weights of polyesters were determined by gel permeation chromatography (GPC; Shimadzu LC-5A instrument, Kyoto, Japan) using polystyrene standards. The terminal carboxyl contents of polyesters were analyzed by titration with N/10 NaOH methanol solution using a mixed indicator (bromothymol blue + phenol red; JIS K6901). The mechanical properties of the cured resins were determined with a Shimadzu autograph AGS-500B universal testing machine. Flexural tests were carried out at a cross head speed of 2 mm/min according to JIS K7203. The fracture toughness, *K_{IC}*, was measured in a three-point bent geometry at a cross head speed of 1 mm/min (ASTM E-399). The glass transition temperatures (*T_gs*) of both polyesters and cured resins were measured as the onset temperatures by differential scanning calorimetry (DSC; Shimadzu DSC 60 type) at a heating speed of 10°C/min under nitrogen. Scanning electron micrographs (SEM) were taken with a combined microanalyzer (JEOL, JXA-8900RL, Tokyo, Japan) using failed specimens in the *K_{IC}* tests. Dynamic viscoelastic analysis was performed with a Rheometrics RDS-II type (Rheometrics Company, Tokyo, Japan) between -150 and 250°C at a heating speed of 5°C/min and a frequency of 1 Hz.

Curing Procedure

The aromatic polyester was dissolved in a mixture of the epoxy resin and the curing agent without solvents by heating at 100°C. Then, the curing accelerators composed of benzyl dimethylamine (1 phr) and 1,2-ethanediol (1 phr) were added to the mixture at 60°C. The resulting clean mixture was poured into a mold that had been preheated to 100°C. The mold consisted of one pair of upright and metal clip-held glass plates spaced by a U-shaped silicon rubber stick; specimens planks with >7 mm thickness were obtained. MHHPA was added stoichiometrically to the epoxy resin.

Table I Characterization of the Polyesters

| Entry No. | Composition ^a (mol %) | M_{GPC}^b (10^3) | M_n^b (10^3) | M_w/M_n | T_g^c (°C) | Acid Content (meq/g) |
|-------------|-------------------------------------|----------------------------------|-----------------------|-----------|-----------------|-------------------------|
| PEP series | | | | | | |
| PEP 04 | — | 5.5 | 3.8 | 1.6 | 30 | 0.025 |
| 05 | — | 7.4 | 4.8 | 1.6 | 30 | 0.024 |
| 03 | — | 12.7 | 7.6 | 1.8 | 31 | 0.043 |
| 01 | — | 23.7 | 14.5 | 1.7 | 35 | 0.057 |
| PEPT series | | | | | | |
| PEPT 01 | TP ^d 48 | 6.6 | 4.5 | 1.6 | 41 | 0.024 |
| 05 | 51 | 6.7 | 4.4 | 1.7 | 52 | 0.116 |
| 04 | 53 | 12.0 | 7.0 | 1.8 | 59 | 0.017 |
| 02 | 53 | 12.4 | 7.1 | 1.9 | 51 | 0.020 |
| 03 | 53 | 17.7 | 9.5 | 1.9 | 51 | 0.069 |

^a Molar ratio.^b By GPC.^c By DSC.^d Terephthalate unit.

The curing cycle was 100°C for 2 h + 160°C for 4 h + 180°C for 2 h. The conversion of epoxy groups was ~96% under these curing conditions, as determined by FTIR (where the CH stretching band at 2995 cm⁻¹ was used as a reference band and the C—O stretching band at 795 cm⁻¹ was used for the epoxy groups). The amount (wt %) of the aromatic polyester used was based on the epoxy resin matrix (DGEBA + MHPHA).

RESULTS

Characterization of Aromatic Polyesters

PEP and PEPT were prepared in quantitative yield by polycondensation of 1,2-ethanediol and aromatic dicarboxylic acids (phthalic anhydride and terephthalic acid) as reported previously.²⁵ Some characteristic properties of the aromatic polyesters are reported in Table I. The GPC average molecular weight (M_{GPC}), obtained from the peak position of GPC curve, was a measure of the molecular weight (MW) in this paper and also in the previous papers^{25–27} because the number-average molecular weight is highly sensitive to the presence of a small amount of lower-molecular-weight materials.

Mechanical and Thermal Properties of Modified Epoxy Resins

The cured parent epoxy resin was transparent, but the modified resins changed from transparent

to translucent during curing, depending on polyester structure and concentration. Representative results for the modification of the epoxy resin are shown in Table II. The mechanical and thermal properties of the modified resins as a function of concentration of polyesters are shown in Figure 1. The K_{IC} value for the modified resin increased with increasing PEP (MW, 7400) concentration up to 20 wt % inclusion and then leveled off: the K_{IC} increased 130% on 20 wt % inclusion of PEP (MW, 7400). Flexural strength for the modified resin was comparable to that for the unmodified resin. Flexural moduli for the modified resins increased linearly with the increase in PEP concentration. It is noteworthy that flexural moduli for the modified resins were significantly higher than that for the unmodified resin. The T_g values decreased slightly compared with that for the unmodified resin on PEP inclusion. When using PEPT (TP 50 mol % unit; MW, 12,400) as a modifier, the K_{IC} for the modified resin increased linearly with increasing PEPT concentration, while flexural strength decreased on 20 wt % inclusion: the morphology of the PEPT (20 wt %)-modified resin changed into phase-inverted structure, as shown later. Unexpectedly, the T_g values for the PEPT-modified resins were slightly lower than those for the PEP-modified materials.

The dependence of the mechanical and thermal properties of the modified resins on polyester MW on 20 wt % inclusion is shown in Figure 2. When using PEP as the modifier, the K_{IC} for the modified resin increased with increasing PEP MW and

Table II Physical Properties of Modified Epoxy Resins

| Entry No. | Polyester | | | | K_{IC}^b (MPa · m ^{1/2}) | n^c | Flexural Properties | | T_g^d (°C) | |
|-------------|------------------|------------------------|--------------------------|------------------|---|-------|--------------------------------|-------------------------------|-----------------|----------------|
| | No. ^a | Composition (mol %) | MW (10 ³) | Concn. (wt %) | | | Strength ^b (MPa) | Modulus ^b (GPa) | | |
| Control | — | — | — | — | 0.51 ± 0.03 | 7 | 152 ± 14 | 3.21 ± 0.07 | 6 | 186 |
| PEP series | | | | | | | | | | |
| CP4 | PEP04 | — | 5.5 | 20 | 0.97 ± 0.07 | 8 | 118 ± 4 | 3.43 ± 0.08 | 7 | — ^e |
| 6 | PEP05 | — | 7.4 | 10 | 0.72 ± 0.05 | 8 | 164 ± 7 | 3.58 ± 0.03 | 6 | 177 |
| 8 | PEP05 | — | 7.4 | 15 | 0.82 ± 0.03 | 7 | 156 ± 15 | 3.68 ± 0.06 | 7 | 180 |
| 5 | PEP05 | — | 7.4 | 20 | 1.16 ± 0.05 | 7 | 161 ± 15 | 3.90 ± 0.05 | 5 | 177 |
| 7 | PEP05 | — | 7.4 | 25 | 1.13 ± 0.10 | 6 | 158 ± 4 | 3.94 ± 0.18 | 6 | 174 |
| 3 | PEP03 | — | 12.7 | 20 | 1.08 ± 0.12 | 8 | 126 ± 5 | 3.34 ± 0.03 | 7 | 182 |
| 1 | PEP01 | — | 23.7 | 20 | 1.18 ± 0.05 | 6 | 71 ± 3 | 2.19 ± 0.07 | 6 | 191 |
| PEPT series | | | | | | | | | | |
| CPT1 | PEPT01 | TP 50 | 6.6 | 20 | 1.08 ± 0.04 | 7 | 156 ± 6 | 3.71 ± 0.04 | 7 | 168 |
| 4 | PEPT04 | 50 | 12.0 | 20 | 1.20 ± 0.06 | 7 | 161 ± 3 | 3.52 ± 0.07 | 7 | 170 |
| 6 | PEPT02 | 50 | 12.4 | 10 | 0.76 ± 0.03 | 7 | 142 ± 17 | 3.43 ± 0.03 | 6 | 173 |
| 7 | PEPT02 | 50 | 12.4 | 15 | 0.93 ± 0.02 | 7 | 142 ± 8 | 3.41 ± 0.06 | 5 | 171 |
| 2 | PEPT02 | 50 | 12.4 | 20 | 1.00 ± 0.06 | 11 | 116 ± 10 | 3.63 ± 0.05 | 10 | 168 |
| 3 | PEPT03 | 50 | 17.5 | 20 | 1.00 ± 0.02 | 7 | 106 ± 7 | 3.28 ± 0.05 | 6 | 170 |

^a Entry number in Table I.^b The ± x values show standard deviation.^c Number of specimens tested.^d By DSC.^e Not obtained by DSC.

leveled off. Flexural strength for the PEP-modified resins decreased with increasing MW of the PEP. Flexural moduli for the modified resins were equal or larger than that for the unmodified resin up to a MW of 12,700, but the use of 20 wt % higher MW (23,700) PEP led to a substantial decrease in flexural modulus. The T_g for the PEP-modified resins was restored with increasing MW of the PEP. Fracture behavior in the PEPT modification was similar to that in the PEP modification. Efficiency of PEPT as a modifier was similar to that of PEP.

Microstructures of the Modified Epoxy Resins

Morphologies of the cured resins were investigated by SEM. The parent epoxy resins were transparent and had only one phase (Figure 3a). When using 10 wt % PEP (MW, 7400), the modified resin became translucent and a small amount of particles (<1 μm in diameter) was observed. The fracture surface of the modified resin became rougher with increasing concentration of the same modifier and a larger amount of ill-defined particles was also ob-

served (Figure 3c and 3d). The morphologies of the modified resins changed considerably, depending on MW of the PEP on 20 wt % inclusion (Figure 4). When using PEP with MW <7400, the modified resin had a particulate structure (Figures 3c and 4a). The morphology of the modified resin became a cocontinuous phase structure on 20 wt % inclusion of PEP (MW, 12,700): the matrix-rich phases are flat and dark, and the modifier-rich ones are composed of a cluster of light particles (Figure 4b). The modifier-rich phases could not be etched out fully by CHCl₃ (25 min at room temperature), perhaps because of improvement in adhesion between the two phases by chemical blending, although particles dispersed in the epoxy matrix could be removed (Figure 4c). Etching was carried out under a mild condition because the modified resin was highly sensitive to etching by CHCl₃ and broken into pieces by immersing in CHCl₃ overnight. It is noteworthy that the parent-cured epoxy resin also has poor solvent resistance. The modified resin had phase-inverted structure on 20 wt % inclusion of PEP (MW, 23,700; Figure 4d), and connected globules in the etched surfaces were

observed (after etching for 10 min at room temperature; Figure 4e).

The SEMs of the PEPT-modified resins are shown in Figure 5. The morphology of the modified resin depended on PEPT concentration. When using 10 wt % PEPT (50 mol % TP unit; MW, 12,400), the modified resin had a particulate structure and the particle phases were a cluster of smaller particles (Figure 5a). The use of 15 wt % of the same polyester led to a cocontinuous phase structure (Figure 5b). Furthermore, the morphology of the modified resin became a phase-inverted structure on 20 wt % inclusion of the same modifier (Figure 5c).

The MW dependence of morphologies for the PEPT-modified resins on 20 wt % inclusion is shown in Figure 6. When using PEPT (MW, 6600), a small number of particles were observed, although the SEM micrograph was obscure (Figure 6a): the dynamic viscoelastic analysis indicates that the modified resin has a phase-sepa-

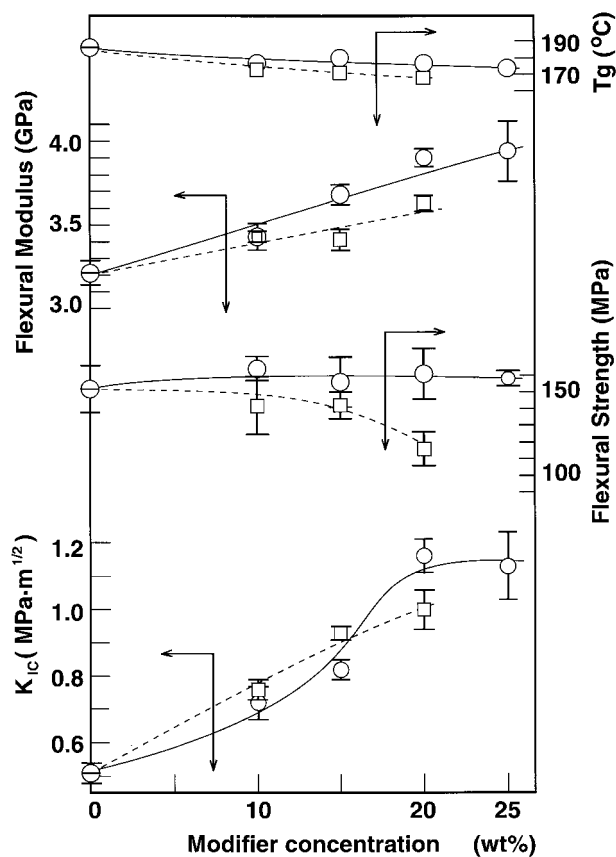


Figure 1 Physical properties of the modified resins as function of polyesters concentration. Key: (⊖) control; (○) PEP (MW, 7400); (□) PEPT (50 mol % TP unit; MW, 12,400).

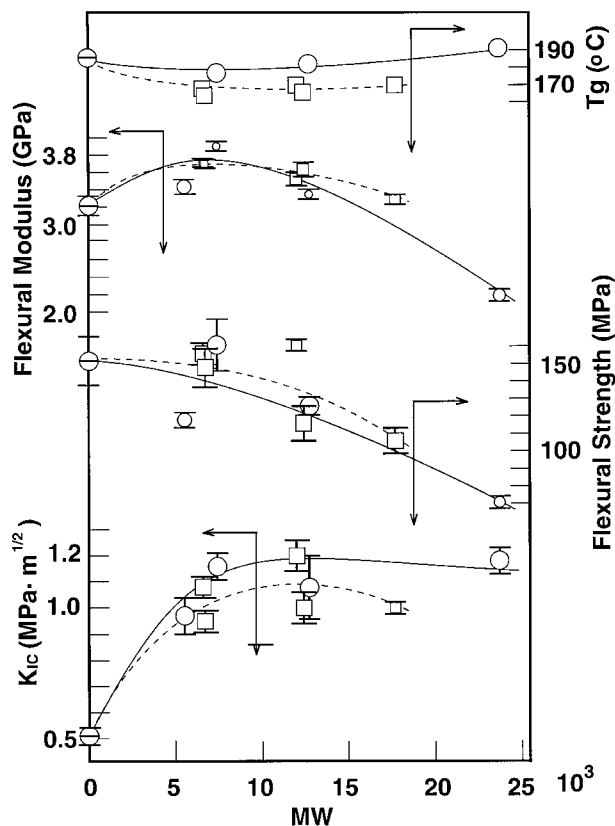


Figure 2 Dependence of physical properties for the modified resins on polyesters molecular weight. Modifier 20 wt % inclusion. Key: (⊖) control; (○) PEP; (□) PEPT (50 mol % TP unit).

rated structure (vide infra). In the modification with PEP with a MW of 12,000, the morphology of the modified resin was rather unclear and might be intermediate between cocontinuous phase and phase-inverted structures (Figure 6b): a slight increase in MW (12,000 to 12,400) of the modifier may accelerate the phase separation between the modifier and the epoxy matrix (Figures 5c and 6b). The use of a high MW (17,700) led to a phase-inverted morphology (Figure 6c).

Dynamic viscoelastic analysis can give information on the microstructures of cured resins. The storage modulus, G' , and $\tan \delta$ curves for the unmodified and PEP-modified resins are shown in Figure 7. In the modification with 10 wt % PEP (MW, 7400), the peak position of the α -relaxation in the $\tan \delta$ curve shifted slightly towards lower temperature and the magnitude of the $\tan \delta$ curve increased considerably in the region from room temperature to the α -relaxation peak temperature, compared with dynamic viscoelastic behavior for the unmodified epoxy resin. The increase in

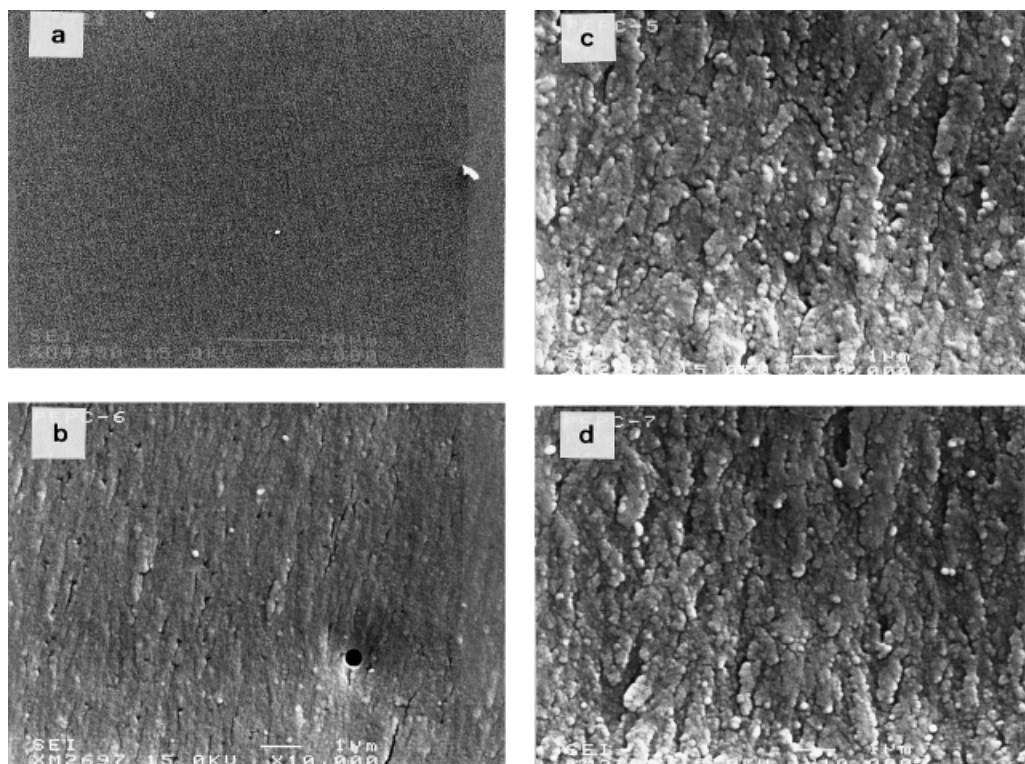


Figure 3 SEMs of fracture surfaces for PEP-modified resins. PEP (MW, 7400): (a) control; (b) 10 wt % inclusion; (c) 20 wt % inclusion; (d) 25 wt % inclusion.

the magnitude of the $\tan \delta$ curve above room temperature indicates the complexity of the matrix structure, which would be because of PEP incorporating into the network. The magnitude of the $\tan \delta$ curve above room temperature increased with increasing PEP concentration to a greater extent. When using 20 wt % of the same modifier, a new relaxation peak (α' -relaxation) was observed at 57°C. The α' -relaxation appeared at 59°C on 25 wt % inclusion. The storage modulus for the PEP 10 wt %-modified resin was smaller than that for the unmodified resin, while the moduli were restored on >20 wt % inclusion.

The MW dependence of dynamic viscoelastic behaviors of the PEP-modified resins on 20 wt % inclusion are shown in Figure 8. The peak positions of the α -relaxation shifted toward higher temperature with increasing MW of PEP. A significant increase in the magnitude of the $\tan \delta$ curve above room temperature was also observed. The magnitude of the α' -relaxation became larger with increasing MW of PEP, indicating that the phase-separation of the modified resin became more significant.

The dynamic viscoelastic behaviors for the unmodified and PEPT-modified resins are shown in

Figure 9. In the modification with 10 wt % PEPT (MW, 12,400), the peak position of the α -relaxation in the $\tan \delta$ curve hardly changed and the magnitude of the $\tan \delta$ curve increased slightly in the region from room temperature to the α -relaxation peak temperature, compared with dynamic viscoelastic behavior for the unmodified epoxy resin. A new relaxation peak (α' -relaxation) was observed at 58°C. The magnitude of both the $\tan \delta$ curve above room temperature and the α' -relaxation peak increased with increasing PEPT concentration. The storage moduli at room temperature were comparable to that of the unmodified resin.

The MW dependence of dynamic viscoelastic behaviors of the PEPT-modified resins on 20 wt % inclusion is indicated in Figure 10. The α -relaxation positions of the modified resin shifted slightly toward higher temperature with increasing MW of PEPT compared with that of the unmodified resin. The extent of the increase in the $\tan \delta$ curve above room temperature was independent of MW of PEPT, whereas the magnitude of the α' -relaxation peak increased with increasing MW of PEPT. The storage moduli at room temperature were comparable to that of the unmodified

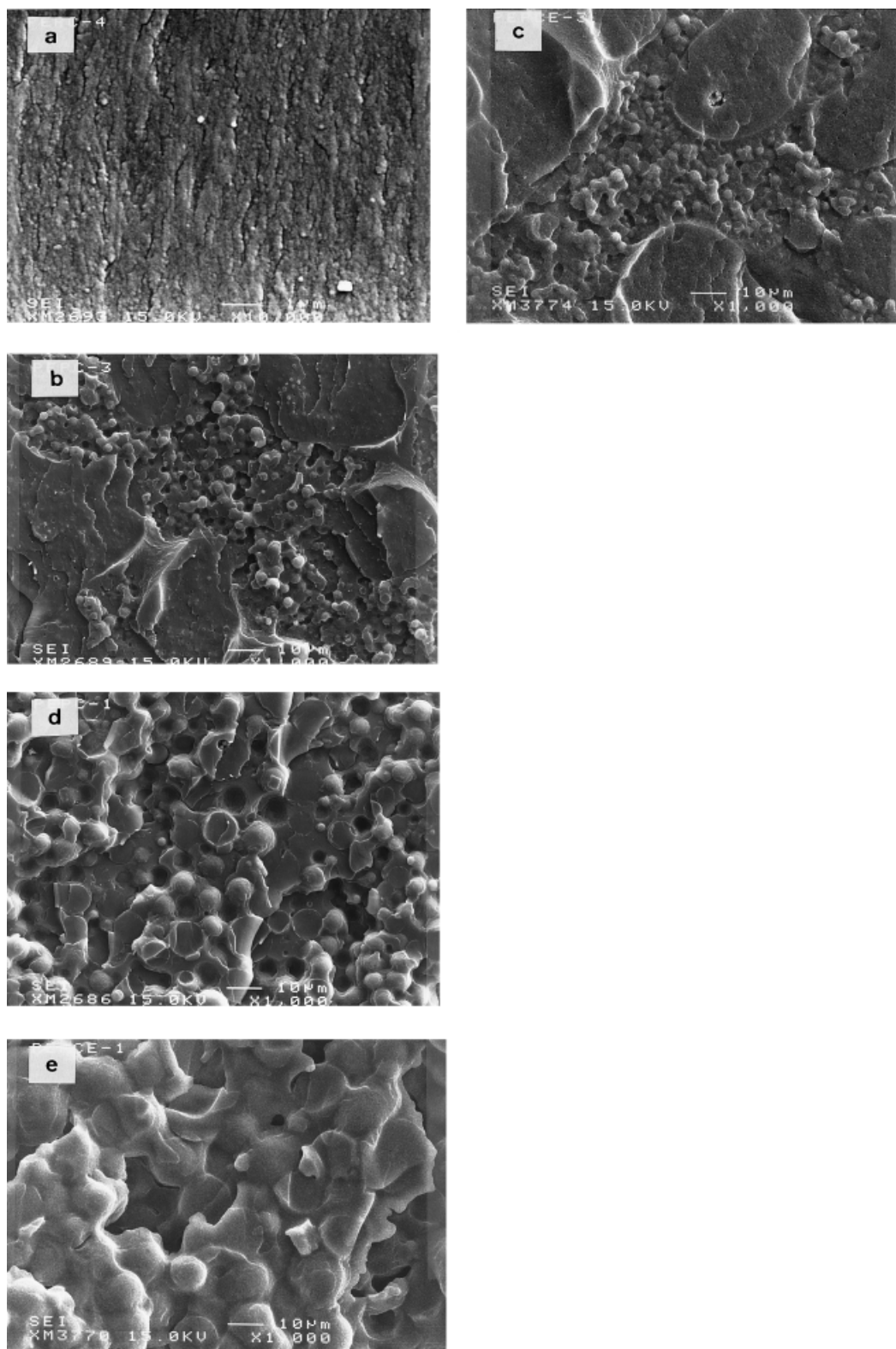


Figure 4 SEMs of fracture surfaces for PEP-modified resins. PEP 20 wt % inclusion. (a) MW 5500; (b) MW 12,700; (c) MW 12,700, after etching (25 min at room temperature); (d) MW 23,900; (e) MW 23,900, after etching (10 min at room temperature).

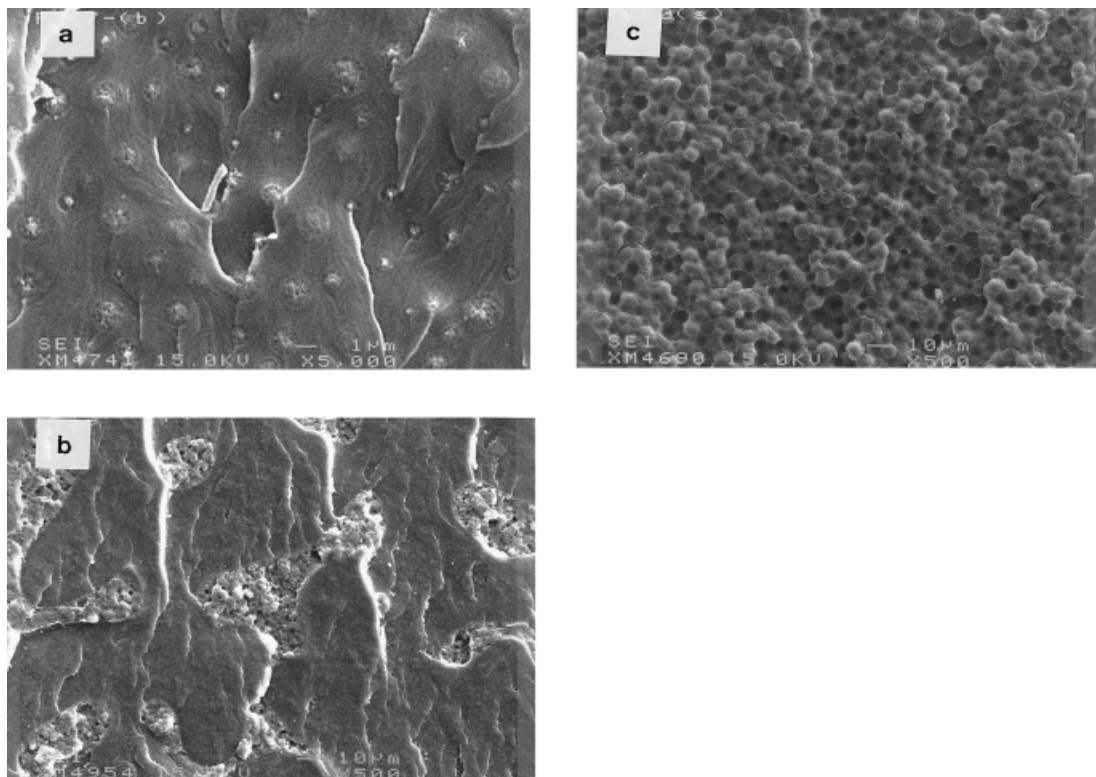


Figure 5 SEMs of fracture surfaces for PEPT-modified resins. PEPT (MW 12,400): (a) 10 wt % inclusion; (b) 15 wt % inclusion; (c) 20 wt % inclusion.

fied resin. These dynamic viscoelastic behaviors correspond to the morphologies of the modified resins.

DISCUSSION

PEP and related copolyester are effective modifiers for improving the brittleness of the acid anhydride-cured cycloaliphatic epoxy resins. The polyesters used in this study were soluble in the epoxy resin without solvents. The use of 20 wt % PEP (MW, 7400) led to a 130% increase in K_{IC} at no expense of its mechanical and thermal properties. The toughening mechanism can be explained in terms of the morphological and dynamic viscoelastic behaviors.

It is well known that the toughening of epoxy resins can be achieved because of the microphase-separation structure of the cured resin in the modification of epoxy resins with reactive liquid rubbers.¹ The elastomer particles with a diameter of a few microns were dispersed in the epoxy matrix in the more effective modification systems. The toughening in the modification with elas-

tomers could be attained by dissipating the fracture energy mainly because of two processes: (1) the formation of shear band of the matrix near the crack based on the deformation of the dispersed particles as stress concentrators and the following crack blunting, and (2) particle elongation and tearing during propagation of the crack with crack deflection and bifurcation.

In the modification of epoxies with engineering thermoplastics, the most effective results can be obtained by the cocontinuous phase or phase inversion structures: the toughening of epoxies could be achieved by the absorption of the fracture energy due to ductile drawing and tearing of the thermoplastic continuous phase.^{3,12-14} We have also reported that thermoplastics such as poly(phthaloyl diphenyl ether) and *N*-phenylmaleimide-styrene copolymers were effective modifiers and that the toughening of epoxies could be attained because of the cocontinuous phase structure.^{16,20-24}

PEP, PBP, and related copolyesters were effective modifiers for highly cross-linked epoxies [the DGEBA/4,4'-diaminodiphenyl sulfone (DDS) system] as reported previously,^{26,27} and the toughen-

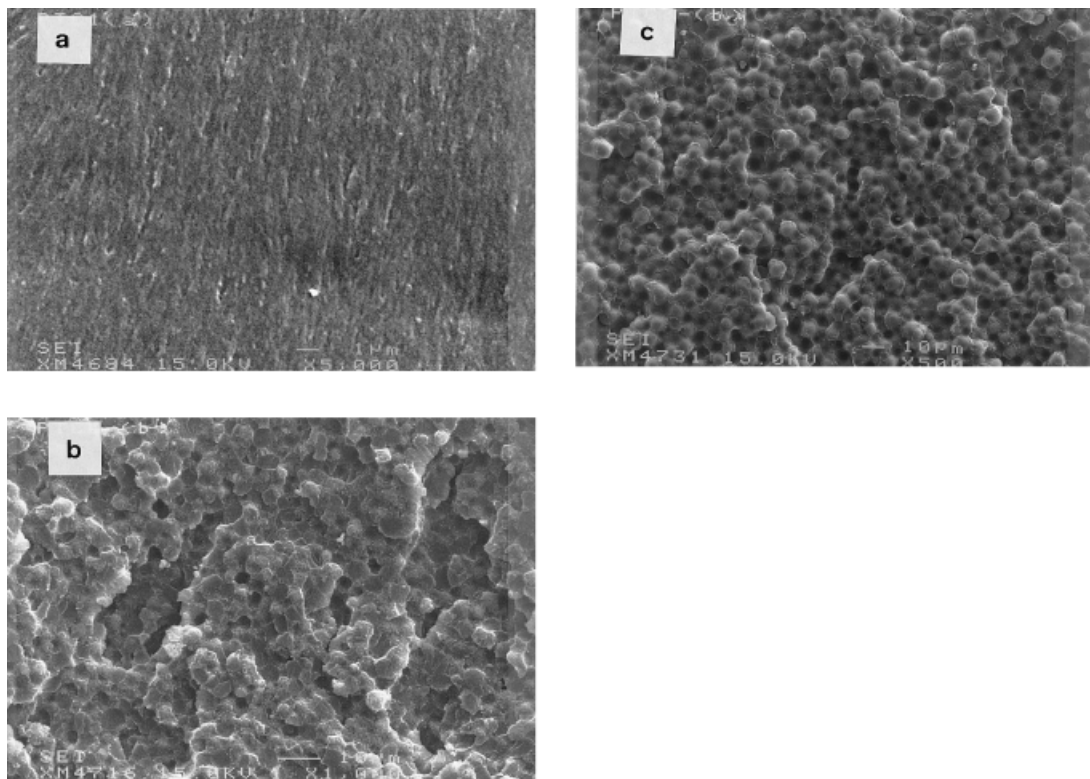


Figure 6 SEMs of fracture surfaces for PEPT-modified resins. PEPT 20 wt % inclusion. (a) MW 6600; (b) MW 12,000; (c) MW 17,700.

ing mechanism was discussed in detail. It was thought that the toughening of epoxies in the modification with PEP, PBP, and related copolyesters would be achieved by the particulate struc-

ture and that three factors would act mainly to improve the brittleness of epoxies: (1) the reinforcement of the matrix itself by incorporation of the polyesters, (2) the high extent of fine poly-

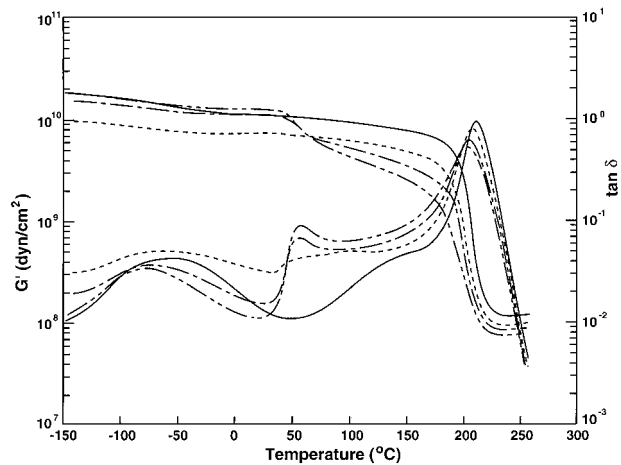


Figure 7 Dynamic viscoelastic analysis for unmodified and PEP-modified resins. PEP (MW, 7400): (—) control; (----) 10 wt % inclusion; (- - -) 20 inclusion; (- - - -) 25 wt % inclusion.

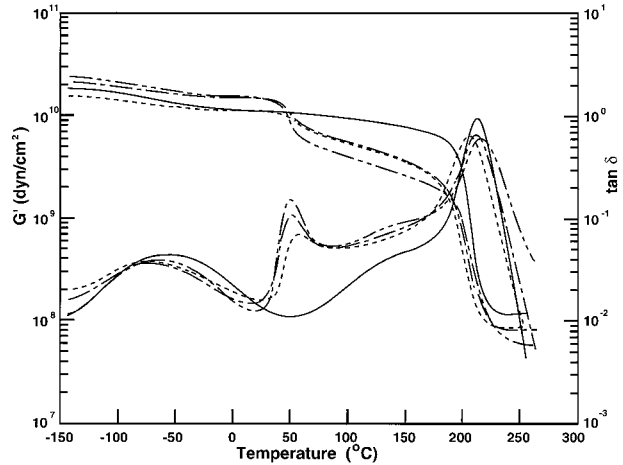


Figure 8 Molecular weight dependence of dynamic viscoelastic analysis for PEP-modified resins. PEP 20 wt % inclusion: (—) control; (----) MW 7400; (- - -) MW 12,700; (- - - -) MW 23,700.

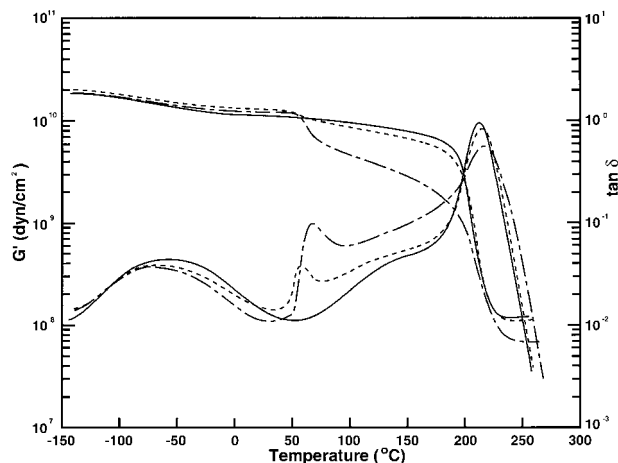


Figure 9 Dynamic viscoelastic analysis for unmodified and PEPT-modified resins. PEPT (MW, 12,400): (—) control; (----) 10 wt % inclusion; (- - -) 20 wt % inclusion.

ter-rich particles, and (3) the existence of the new relaxations based on the polyesters at ambient or slightly higher temperatures.

In the modification of highly cross-linked epoxies with PEP, PBP, and related copolyesters, most of the modified resins have particulate morphologies with well-defined fine spherical particles ($<1 \mu\text{m}$ in diameter) dispersed in the matrix, and the particles size distribution was also small. In the modification of the MHHPA-cured DGEBA resin (lightly cross-linked epoxies) by PEP, the modified resins also had particulate structures.²⁵ Recently, we prepared poly(1,4-cyclohexanedimethylene phthalate) and used as a modifier for the DDS-cured DGEBA resin: the toughening could also be achieved because of the particulate structure of the modified resin.³¹ The cocontinuous phase or phase-inverted structures have not been observed at all in the previous studies.^{25-27,31}

The parent MHHPA-cured cycloaliphatic epoxy resin is among highly cross-linked epoxies, considering the high T_g value (186°C) of the cured material. In the modification of cycloaliphatic epoxies by PEP and PEPT, the morphologies of the modified resins changed drastically: the cocontinuous phase or phase-inverted structures could be observed, depending on the polyester structure and concentration (Figures 3–6). The dependence of morphological behaviors on the structure of epoxy resins can be explained in terms of the solubility parameter (δ) to some extent; the δ values ($(\text{MJ}/\text{m}^3)^{1/2}$ for Celoxide 2021™, DGEBA, PEP, and PEPT are 18.04, 21.68, 25.40, and 23.53, re-

spectively (by Fedors' method³²). The δ values of the Celoxide 2021/MHHPA, the DGEBA/MHHPA and the DGEBA/DDS systems are 18.55, 19.76 and 24.80, respectively, considering the curing agents. The δ value indicates that the cycloaliphatic epoxy resin has lower miscibility with the polyesters than does the DGEBA epoxy material. This result reflects the change in morphologies of the modified resins. Although the morphologies of the modified cycloaliphatic epoxy resins depended on the polyester structure and concentration, the particulate structure was most suitable to improve the brittleness of the cured resin in the present PEP modification as follows. When using 20 wt % PEP (MW, 7400), the modified resin had the particulate structure (Figure 3c) and the K_{IC} value increased 130%, with no deterioration of flexural properties (Table II, no. CP5). In contrast, the modified resin became the cocontinuous phase structure by using 20 wt % of higher MW (12,700) PEP (Figure 4b) and the K_{IC} value increased 110% at a slight expense of flexural strength (Table II, no. CP3). Furthermore, when the modified resin had the phase-inverted structure (Figure 4e) with inclusion of 20 wt % PEP (MW, 23,700), its flexural strength decreased considerably with the increase in the K_{IC} value (Table II, no. CP1).

The relation between modification behavior and morphology in the PEPT modification was complicated compared with that in the PEP modification. It is thought that most suitable morphology may be a particulate structure, consider-

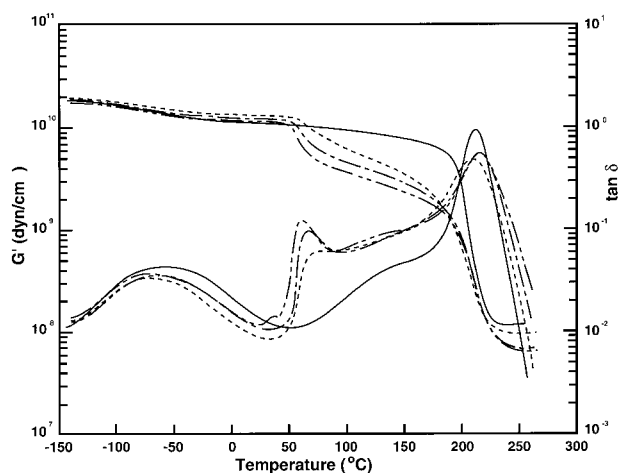


Figure 10 Molecular weight dependence of dynamic viscoelastic analysis for PEPT-modified resins. PEPT 20 wt % inclusion: (—) control; (----) MW 6600; (- - -) MW 12,000; (· · ·) MW 17,700.

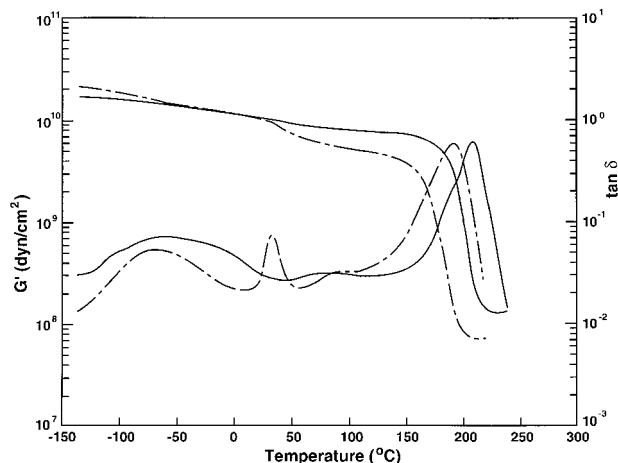


Figure 11 Dynamic viscoelastic analysis in the modification of the DDS-cured DGEBA resin by PEP. Key: (—) control; (---) PEP (MW, 8100) 20 wt % inclusion.

ing the present PEP modification and the previous results.^{25–27,31} When using 20 wt % low MW (6600) PEPT, the modified resin had the particulate structure (Figure 6a) and the K_{IC} value increased 110% with no deterioration of flexural properties (Table II, no. CPT1). However, the use of moderate MW (~12,000) PEPT could not generate a particulate structure (Figure 5c and 6b). Furthermore, inclusion of similar MW PEPT at 20 wt % led to confusing modification results: the use of 20 wt % PEPT (MW 12,000) led to 135% increase in K_{IC} , with no loss of flexural properties, whereas K_{IC} increased 100% with a 20% decrease in flexural strength on inclusion of 20 wt % PEPT (MW 12,400; Table II, nos. CPT4 and CPT2) and their morphologies were different from each other. These results might be based on the heterogeneity of the modified resins in the present modification, especially in the PEPT modification system, possibly because of low miscibility of the polyesters with the cycloaliphatic epoxy matrix.

Dynamic viscoelastic analysis indicates that PEP- and PEPT-modified cycloaliphatic epoxy resins would phase-separate to a greater extent than do the PEP-modified MHHFA-cured or DDS-cured DGEBA resins;^{25,26} the magnitude of the α' -relaxation peak in the former resins is much larger than that in the latter materials. Also, the increase in the $\tan \delta$ curve above the α' -relaxation temperature in the former system is far greater than those in the latter systems. The dynamic viscoelastic behavior in the modification of the DDS-cured DGEBA resin by PEP is shown in

Figure 11 for comparative purposes.²⁶ This comparison indicates that the matrix compositions in the former system would become more complicated than those in the latter because of incorporation of lower miscible polyesters into the epoxy matrix by chemical blending. It is noteworthy that the curing agent is the acid anhydride and that the polyesters used have terminal hydroxyl and carboxyl groups (Table I). It is thought that the improvement in the brittleness of the matrix itself could be attained especially by the incorporated polyesters in the present modification.

The existence of the α' -relaxation near room temperature is one of the most important factors to reduce the brittleness of epoxies. When using PEP, PBP, and related copolyesters as modifiers in the DGEBA/DDS systems, the α' -relaxation peaks based on the modifiers were observed in the region of T_g of the aromatic polyesters by dynamic viscoelastic analysis. The α' -relaxation peak was also observed in the present modification. It is reported that the presence of the relaxation peak near room temperature was effective in improving the toughness of the epoxy resin because of the increase in the plastic deformation zone attributed to the increase in temperature at the crack front.^{33,34} We also reported that several relaxations at $>50^\circ\text{C}$ contribute to toughening of epoxies in the modification of the DDS-cured DGEBA resins with butyl acrylate-glycidyl acrylate copolymers.³⁵

Therefore, the toughening of epoxies in the present PEP modification would be achieved because of the three factors just mentioned and also in the modification of the DDS-cured DGEBA resins by the PEP and related polyesters. Particulate and cocontinuous phase structures might be suitable to improve toughness in the PEPT modification.

The T_g values for the modified resins were equal or slightly low compared with that for the parent resin.

CONCLUSIONS

PEP and PEPT (50 mol % TP unit) were effective modifiers for improving the toughness of cycloaliphatic epoxy resins. Their effectiveness depended on polyester structure, MW, and content. The toughening mechanism in the PEP modification is due to the particulate structure and also in the modification of the DDS-cured DGEBA resin by the PEP and related (co)polyesters. Efficiency

of PEP as the modifier would be because of three causes: (1) the reinforcement of the matrix itself by the incorporated polyesters; (2) the existence of the new relaxations based on the polyester and the broadness of the α -relaxation peak; and (3) the dispersion of fine polyester-rich particles. In the PEPT modification system, particulate and cocontinuous phase structures might be suitable to improve toughness. The more suitable compositions for the modification of the epoxy resin were inclusion of 20 wt % PEP (MW, 7400), where K_{IC} increased 130% with no loss of mechanical and thermal properties.

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