Toughening of Epoxy Resins by Modification with Aromatic Polyesters

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SYNOPSIS

Aromatic polyesters, prepared by the reaction of phthalic or isophthalic acids and α,ω-alkanediols, were used to reduce the brittleness of bisphenol-A diglycidyl ether epoxy resin cured with methyl hexahydrophthalic anhydride. These polyesters were effective as modifiers for toughening of the epoxy resin system. The most suitable composition for modification of the epoxy resins was inclusion of 20 wt % of poly(ethylene phthalate) (MW 7200), which resulted in a 150% increase in the fracture toughness (K_{IC}) of the cured resin at no expense of its mechanical properties. The effectiveness of poly(alkylene phthalate)s as modifiers decreased with increasing the chain length of alkylene units. The toughening mechanism was discussed based on the morphological and dynamic mechanical behaviors of the modified epoxy resin system.

INTRODUCTION

Reactive liquid rubbers[1] or terminally functionalized engineering thermoplastics[2] were used to decrease the brittleness and to improve the toughness of cured epoxy resins.

In a previous paper[3] epoxide-containing acrylic rubbers, prepared by copolymerization of n-butyl acrylate (BA) with vinylbenzyl glycidyl ether (VBGE) or terpolymerization of BA, VBGE, and styrene (St) or acrylonitrile (AN), have been reported to decrease the brittleness of epoxy resins. It is well known in many earlier patents[4] that aromatic polyesters such as modified poly(alkylene terephthalate)s were effective as modifiers of epoxy resins, but there has not been reported a systematic study on the structure–property relations of aromatic polyesters as the modifiers. Especially, it is technologically interesting to evaluate aromatic polyesters as modifiers of epoxy resins on the viewpoint of fracture mechanics. Recently fracture toughness (K_{IC}) has been used as a measure of toughness of cured resins.

This paper reports the modification of methyl hexahydrophthalic anhydride (MHHPA)-cured epoxy resins (diglycidyl ether of bisphenol A, DGEBA) with aromatic polyesters. The aromatic polyesters, soluble in the epoxy resin without using solvents, were prepared by the reaction of phthalic or isophthalic acids and α,ω-alkanediols. The effect of the structure, the molecular weight, and the amount of the polyesters added on the properties of the modified epoxy resin was examined based on the fracture toughness (K_{IC}) of the cured resin.

EXPERIMENTAL

Materials

The epoxy resins used were the liquid bisphenol-A type epoxy resin (DGEBA) [Epikote 828, Shell Chemical Co., epoxy equivalent weight (EEW) 190]. Methyl hexahydrophthalic anhydride (MHHPA) (Epiclon B-650, Dainippon Ink and Chemical Inc.) was used as a curing agent without further purification. Other reagents were used as received.

Measurements

Molecular weights of polyesters were determined by gel permeation chromatography (Shimadzu LC-5A

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instrument) using polystyrene standard calibration or by viscometry. Glass transition temperatures of both polyesters and cured resins were measured by differential scanning calorimetry (Shimadzu DSC 41M type). The terminal carboxyl contents of polyesters were analyzed by titration with N/10 NaOH methanol solution using a mixed indicator (bromothymol blue + phenol red) as an indicator (JIS K6901). Mechanical properties of cured resins were measured with a Shimadzu S-500 universal testing machine. Tensile strength and modulus (JIS K7113) of cured resins were determined using rectangular specimens at a cross head speed of 1 mm/min. Fracture toughness (K_{IC}, ASTM E-399) was measured in a three-point bent geometry at a crosshead speed of 1 mm/min. Scanning electron micrographs were taken with a JEOL JSM 35 instrument using failed specimens in the K_{IC} tests. Dynamic mechanical analysis was performed with a DuPont DMA 982 instrument between −130 and 210°C at a heating speed of 5°C/min at variable frequency of 30–2 Hz.

Preparation of Aromatic Polyesters

Polyesters were prepared by the reaction of phthalic or isophthalic acids and α,ω-alkanediols according to a patented procedure.[5] α,ω-Alkanediols were 1,2-ethane, 1,4-butane, and 1,6-hexanediols.

Typical procedures are shown as follows: Titanium tetrachloride 5 mL was added into water below 10°C. The reaction mixture was adjusted to pH 8–9. The resulting white precipitate was filtered, washed with water, and used as a catalyst of esterification. A 200-mL four-necked flask was charged with 1,4-butanediol [67.5 g (0.75 mol)] and the catalyst (0.15 g), and stirred to disperse the catalyst. Then phthalic anhydride 116.7 g (0.78 mol) was added. The reaction mixture was stirred at 220°C for 90 min followed by heated to 245°C with evacuating gradually to 1 mm torr and kept at 245°C for 2 h. The obtained polymer was purified by reprecipitation with acetone/methanol. Yield = 139.0 g; M_{GPC} = 7000.

Curing Procedure

A mixture of the epoxy resin and polyesters was heated at 80–95°C for about 1 h to homogenize, and the curing agent, MHHPA, was added into the mixture, which was kept at 90°C for 30 min to homogenize and degas, and then an accelerator, benzyldimethylamine (BDMA), was added and stirred gently to minimize air entrapment for 3 min. The resulting clean mixture was poured into a silicon

mold preheated at 85°C and cured at 85°C for 5 h followed by post-curing at 150°C for 15 h. The composition of the parent epoxy resin is as follows: Epikote 828/MHHPA/BDMA = 100/88/1 (wt ratio). The amount (wt %) of polyester used was calculated based on the epoxy matrix.

RESULTS

Preparation and Characterization of Aromatic Polyesters

Table I shows the results of polycondensation of aromatic carboxylic acids and α,ω-alkanediols. The molecular weights of the aromatic polyesters were controlled by adjusting the mole ratio of the starting materials. Table II summarizes some characteristic properties and abbreviation of the polyesters. The molecular weight of the polyesters were measured by GPC except for poly(butylene isophthalate) (PBI). The polyesters prepared contain a small amounts of lower-molecular-weight products. The number-average molecular weight is highly sensitive to the presence of a small number fraction of lower-molecular-weight material. Then, the GPC-average molecular weight, obtained from the peak position of GPC curve, was used as a measure of the molecular weight. As PBI was insoluble in tetrahydrofuran, the viscosity-average molecular weight was obtained using chloroform as a solvent by the following Mark–Houwink–Sakurada equation[6]:

$$[\eta] = 5.12 \times 10^{-6} \, M_w^{1.09}$$

Poly(ethylene isophthalate) was not used as a modifier owing to its poor solubility in epoxy resin.

Mechanical and Thermal Properties of Modified Epoxy Resins

Figure 1 shows the tensile properties of the cured resins as a function of concentration of the polyester with similar molecular weight (MW). The concentration is expressed in terms of the weight percentage of polyester in the epoxy–polyester mixtures. The cured resins were transparent in every case. The tensile strength for the modified resin did not decrease with increasing poly(ethylene phthalate) (PEP) or poly(butylene phthalate) (PBP) content up to 20 wt %, compared to the cured parent epoxy resin, and then decreased. In the modification of the resin with poly(hexylene phthalate) (PHP) the tensile strength decreased gradually with increasing

Table I Polycondensation of Aromatic Acid and α, ω-Alkanediol

Acid (g/mol)	Diol (g/mol)	Catalyst (g)	Conditions (°C (torr)/min)	Yield (g)	M_{GPC}[a]
Poly(ethylene Phthalate)					
$\dfrac{89.20}{0.60}$	$\dfrac{55.86}{0.90}$	0.02	200/120 + 275(10)/45	101.3	3000
$\dfrac{89.20}{0.60}$	$\dfrac{55.86}{0.90}$	0.05	180/120 + 275(2)/120	121.8	7200
$\dfrac{89.20}{0.60}$	$\dfrac{55.86}{0.90}$	0.10	200/120 + 275(1)/180	113.8	10,100
Poly(butylene Phthalate)					
$\dfrac{89.20}{0.60}$	$\dfrac{64.80}{0.72}$	0.02	220/90 + 245(4)/60	115.3	3100
$\dfrac{116.65}{0.78}$	$\dfrac{67.50}{0.75}$	0.15	220/90 + 245(0.15)/120	139.0	7000
$\dfrac{89.20}{0.60}$	$\dfrac{82.93}{0.92}$	0.10	220/90 + 245(0.2)/120	127.4	8700
$\dfrac{89.20}{0.60}$	$\dfrac{108.00}{1.20}$	0.10	220/90 + 245(4)/220	131.2	15,600
Poly(butylene Isophthalate)					
$\dfrac{83.07}{0.50}$	$\dfrac{72.10}{0.80}$	0.10	220/90 + 245(5.8)/100	102.4	7000[b]
$\dfrac{83.07}{0.50}$	$\dfrac{90.12}{1.00}$	0.10	220/90 + 245(6)/120	97.2	12,500[b]

[a] Obtained from the main peak position of GPC curve.
[b] By viscometry.

PHP content. Figure 2 shows the fracture toughness (K_{IC}) values for the modified resins with standard deviations. The K_{IC} values increased linearly with an increase in the polyester concentration.

Table III shows the mechanical properties of the cured resins on addition of 20 wt % of the poly(alkylene phthalate)s with various MW. In the modification with the polyesters of higher MW (more than ca. 10,000), the tensile strength for the modified resins decreased, though the K_{IC} values increased. The cured parent resin was transparent. The modified resins became translucent using PEP with MW more than 7200. The cured resins were transparent in the modification with both PBP and PHP. The stress whitening was observed in the tensile tests of the resin modified with PBP of MW 15600. The resins were transparent in the modification with both PBI and poly(hexylene isophthal-ate) (PHI). The higher MW PHI (13,200)-modified resin whitened in the tensile tests.

The fracture toughness K_{IC} for the modified resins increased with an increase in MW of the polyesters used. In the modification with PEP of MW less than 7200 the K_{IC} values increased with no expense of their tensile strength. The addition of 20 wt % of PEP (MW 7200) resulted in a 150% increase in the fracture toughness (K_{IC}) at no expense of the mechanical properties. The use of higher MW PEP (10,100) led to a slight decrease in tensile strength. Tensile moduli for the PEP-modified resins were larger than the parent resin. The use of PBP with MW less than 7000 increased the K_{IC} values at no expense of the mechanical properties: The addition of 20 wt % of PBP (MW 7000) led to an 80% increase in the K_{IC} value. The modification, however, with PBP of higher MW (10,200) led to a 110%

Table II   Characterization of Aromatic Polyesters

M_{GPC}[a]	M_n	M_w	M_w/M_n	AC[b] (meq/g)	T_g (°C)
Poly(ethylene Phthalate) (PEP)
3000	2100	3400	1.64	0.012	15
6300	2700	5500	2.03	0.013	22
7200	3200	6500	2.03	0.010	8
10,100	3900	9600	2.46	—	8
Poly(butylene Phthalate) (PBP)
3100	2200	3500	1.54	0.545	-12
4900	3000	5100	1.70	0.214	-6
7000	3400	6500	1.91	0.540	-13
8700	5200	8700	1.68	0.203	-9
10,200	4800	10,100	2.09	—	—
15,600	8600	16,300	1.89	—	-12
Poly(hexylene Phthalate) (PHP)
2600	2000	2600	1.30	—	-25
6300	3400	6200	1.84	0.010	-20
9200	4300	8900	2.08	—	-21
Poly(butylene Isophthalate) (PBI)
(7000)[c]	—	—	—	—	-4
(12,500)[c]	—	—	—	—	-4
Poly(hexylene Isophthalate) (PHI)
6500	4000	6400	1.61	—	—
13,200	7200	13,000	1.80	—	-6

[a] Obtained from the main peak position of GPC.
[b] Acid content.
[c] Viscosity-average molecular weight.

increase in the K_{IC} at a slight expense in tensile strength. The addition of 20 wt % of PHP (MW 6300) resulted in a 70% increase in the K_{IC} at minimal expense of tensile strength.

The modification with 20 wt % of PBI (MW 7000) led to a 70% increase in the K_{IC} at no expense of the tensile properties. The use of higher MW PBI (12,500) resulted in an 110% increase in the fracture toughness at a slight expense of tensile properties. In the modification with 20 wt % of PHI (MW 6500) the extent of expense of tensile strength was larger, compared with the PHP (MW 6300)—or PBI (MW 7000)—modified resins.

Table III also shows the glass transition temperatures T_g's for the resins modified with 20 wt % of the polyesters. Table IV shows the T_g value for the resins modified with various amounts of the polyesters. Two T_g's were observed in the modification

with more than 20 wt % of the polyesters. When the polyester concentration increased, the higher T_g decreased gradually.

Morphologies of the Modified Resins

Figure 3 shows the scanning electron microscope (SEM) of both the cured parent and PEP-modified resins. The unmodified resin has only one phase, and the fracture surface is smooth and featureless up to a magnification of 20,000. The fracture surface for the resin modified with PEP was quite different from that for the parent resin. The fracture surface for the resin modified with 20 wt % of PEP (MW 6300) was a rough one containing ridges, but no particle existed. There were somewhat irregular particles with an average size of 0.13 μm (between 0.07 and 0.20 μm) in the modification with PEP of
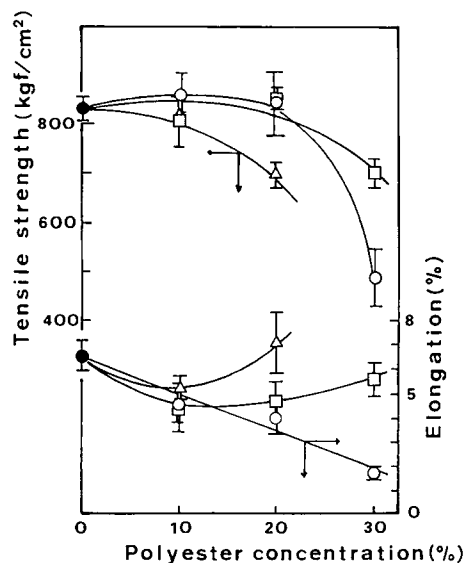
Figure 1   Effect of poly(alkylene phthalate)s concentration on the tensile properties of cured epoxy resins: (●) control; (○) PEP (MW 6300); (□) PBP (MW 7000); (△) PHP (MW 6300).

MW 7200. The volume fraction (0.02) of the dispersed particle for the modification system is much smaller than the weight fraction (0.20) of PEP added in the cured system. On the addition of PEP with MW of 10,100, its particle size increased slightly. Figure 4 shows SEMs of the resins modified with PBP and PHP. No particle existed in the resins modified with PBP (MW 7000), but their fracture surfaces were rough, compared to the parent resin (Fig. 3). The fracture surface for the resin modified with PBP (MW 15,600) tended to macrophase separation. The morphology of the fracture surface for the PHP (MW 6300)-modified resin was similar to that for the PBP (MW 7000) modification system.

Figure 5 shows SEMs of the cured resins modified with poly(alkylene isophthalate). In the modification with PBI the fracture surfaces were rough, but no particle existed [Figs. 5(a) and 5(b)]. The fracture surface for the modification with PHI (MW 6500) was also rough [Fig. 5(c)]. The fracture surface for the modified resin with higher MW PHI (MW 13,200) showed the presence of macrophase-separated structure [Fig. 5(d)].

Dynamic Mechanical Analysis of the Modified Resins

Dynamic mechanical analysis (DMA) can give information on microstructures of cured resins. Figure

6 shows the tensile storage moduli and tan δ curves for the PEP-modified resin. The peak position of the α-relaxation in the tan δ curves for the resin modified with PEP of MW 6300 shifted from 155 to 136°C and its magnitude decreased, compared to the parent resin; then a new lower temperature relaxation (referred to as the α'-relaxation) appeared at ca. 70°C. The tan δ curve for the resin modified with PEP of MW 7200 showed the α-relaxation peak at 139°C and the well-defined α'-relaxation peak at 71°C. In the tan δ curve of the resin modified with higher MW PEP (10,100) the α-relaxation peak position shifted to 147°C, and the α'-relaxation peak position was higher (75°C) and its magnitude larger. The storage modulus for the PEP modified resin increased over the temperature range lower than T_g.

The effect of PEP concentration on dynamic mechanical behavior was investigated in the resin modified with PEP (MW 6300) (Fig. 7). When the PEP concentration increased, the α-relaxation peak position of the tan δ curve became broader and shifted towards lower temperature, compared to the parent resin, and the magnitude of the α'-relaxation peak increased. The increased PEP concentration resulted in the increased tensile storage modulus over the lower temperature range than 60°C. The tensile storage modulus decreased slightly around the α'-relaxation temperature.

Figure 8 shows the molecular weight dependence of tensile storage moduli and tan δ curves for the PBP-modified resin. On addition of PBP with MW less than 8700, the α-relaxation peaks of the tan δ curves became much broader, their peak positions shifted towards far lower temperature, compared to
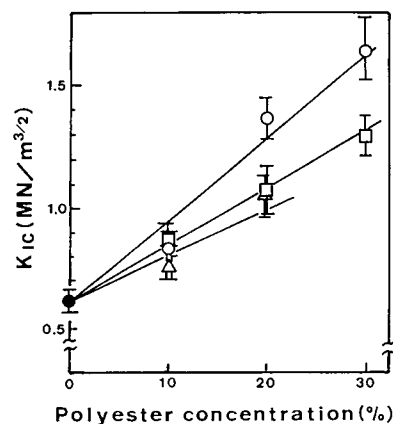

Figure 2   Effect of poly(alkylene phthalate)s concentration on the fracture toughness, K_{IC}, for the cured resins: (●) control; (○) PEP (MW 6300); (□) PBP (MW 7000); (△) PHP (MW 6300).

Table III   Mechanical and Thermal Properties of Poly(alkylene (Iso)phthalate)-Modified Epoxy Resins[a]

Polyester	MW	σ^b (kgf/cm^2)	ϵ^c (%)	E^d (kgf/mm^2)	n^e	K_{IC} (MN/m$^{3/2}$)	n^e	T_g^f (°C)
PEP	3000	896 ± 67	3.4 ± 0.5	364 ± 15	11	1.13 ± 0.06	9	46, 82
	6300	842 ± 72	4.0 ± 0.7	331 ± 11	7	1.37 ± 0.08	12	36, 87
	7200	863 ± 53	4.3 ± 0.9	338 ± 11	6	1.52 ± 0.09	11	34, 91
	10100	707 ± 44	3.0 ± 0.3	320 ± 21	8	1.46 ± 0.09	8	36, 92
PBP	3100	887 ± 42	4.7 ± 0.4	340 ± 13	10	1.07 ± 0.07	8	38, 70
	4900	835 ± 23	4.5 ± 0.6	338 ± 18	14	1.12 ± 0.05	6	38, 71
	7000	853 ± 25	4.7 ± 0.8	330 ± 14	10	1.08 ± 0.10	5	37, 71
	8700	717 ± 19	4.4 ± 0.6	299 ± 15	6	1.29 ± 0.06	4	42, 70
	10200	673 ± 17	6.9 ± 0.8	257 ± 8	7	1.29 ± 0.05	8	40, 92
	15600	581 ± 11	9.4 ± 1.0	221 ± 7	8	1.91 ± 0.14	7	99
PHP	2600	786 ± 29	4.1 ± 0.4	313 ± 17	6	0.90 ± 0.06	5	44, 68
	6300	696 ± 27	7.1 ± 1.3	272 ± 20	11	1.06 ± 0.07	8	38, 73
	9200	573 ± 15	6.2 ± 0.7	226 ± 15	7	1.12 ± 0.05	5	38, 82
PBI	7000	799 ± 34	4.9 ± 0.6	329 ± 15	8	1.02 ± 0.07	6	39, 74
	12500	629 ± 24	5.5 ± 0.9	272 ± 14	6	1.31 ± 0.09	7	91
PHI	6500	586 ± 17	6.5 ± 1.3	266 ± 11	9	1.15 ± 0.04	7	44, 70
	13200	429 ± 18	10.3 ± 2.4	193 ± 9	7	1.87 ± 0.10	8	85
Epikote 828		828 ± 11	6.6 ± 0.6	285 ± 14	6	0.61 ± 0.05	13	99

[a] Epoxy matrix/polyesters = 80/20 (wt ratio). Curing conditions, 85°C/5 h + 150°C/15 h. The ±x values show standard deviations.
[b] Tensile strength.
[c] Elongation at break.
[d] Tensile modulus.
[e] Number of specimen.
[f] From DSC: heating rate, 10°C/min.

the PEP-modified resin (Fig. 6), and no lower temperature relaxation peak emerged. The tensile storage modulus below T_g in the modification with PBP increases slightly, compared to the parent resin. The dynamic mechanical behavior of the cured resin modified with higher MW PBP (15,600) was considerably different from that in the modification with lower MW PBP. The α-relaxation peak became narrower again, its position shifted towards higher temperature, and a new relaxation peak emerged at

46°C. The tensile storage modulus decreased largely, compared to the parent resin.

Figure 9 shows the effect of PBP (MW 7000) concentration on the dynamic mechanical behavior of the modified resin. The larger the PBP concentration, the broader the α-relaxation peak and the lower the peak position; but the α′-relaxation peak did not emerge, and no tendency to phase-separate was observed. The storage modulus around room temperature increased in the use of 30 wt % of PBP.

Table IV   Glass Transition Temperature (T_g) (°C) of Poly(alkylene Phthalate)-Modified Epoxy Resins[a]

Epoxy : Polyester Wt Ratio	Polyester (Molecular Weight)		
	PEP(6300)	PBP(7000)	PHP(6300)
100 : 0	99	99	99
90 : 10	94	89	82
80 : 20	36, 87	37, 71	38, 73
70 : 30	40, 79	36, 63	—

[a] Curing conditions; 85°C/5 h + 150°C/15 h. From DSC: heating rate, 10°C/min.
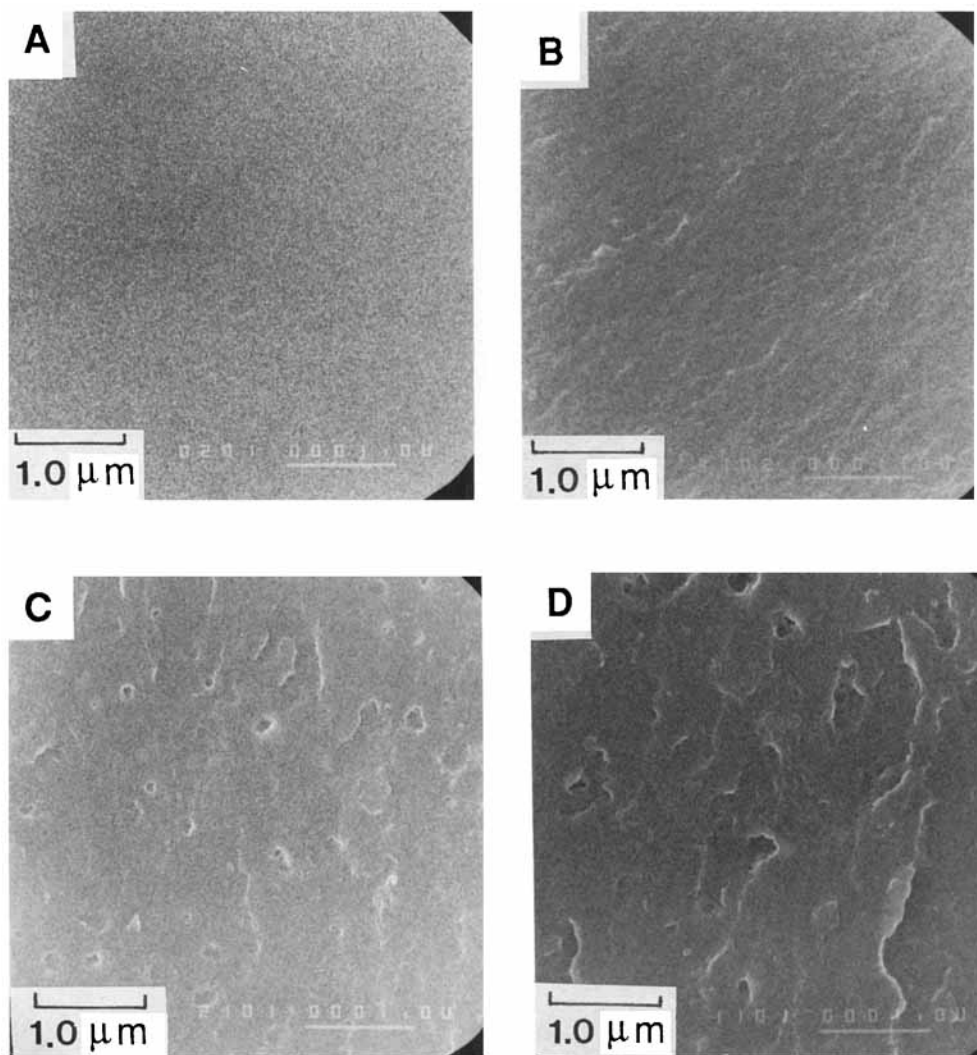
Figure 3 SEMs of fracture surfaces for the cured resins modified with 20 wt % of poly-esters: (A) control; (B) PEP (MW 6300); (C) PEP (MW 7200); (D) PEP (MW 10,100).

DISCUSSION

Poly(alkylene (iso)phthalate)s were effective as modifiers for toughening of the epoxy resin system. The effectiveness of poly(alkylene phthalate) de-creased with increasing the chain length of alkylene units of polyesters, i.e., in the order of PEP > PBP > PHP. Especially, PEP was highly effective and the use of PEP (20 wt %) with MW less than 7200 led to an increase in the K_{IC} value to a large extent at no expense of the mechanical properties. The most suitable composition for modification of the epoxy resins was inclusion of 20 wt % of PEP (MW 7200), which resulted in a 150% increase in K_{IC} of the cured resin (Table III). PBP was less effective

as a modifier than PEP, but the use of the former (20 wt %) with MW 7000 led to an 80% increase in the K_{IC} value with no expense of the mechanical properties. The more interesting modification sys-tem was obtained by the addition of 30 wt % of PBP with MW 7000, where the K_{IC} value increased by 110% at a slight expense (15%) of its tensile strength. These behaviors are very interesting, con-sidering that there is an unavoidable expense of me-chanical properties of cured resins with an increase in K_{IC} in modifications of epoxy resins with reactive elastomers.[1,3] The order of the effectiveness of poly(alkylene phthalate)s can be explained quali-tatively by the solubility parameter (SP); the SP values $(cal/cm^3)^{1/2}$ for the parent epoxy resin, PEP,
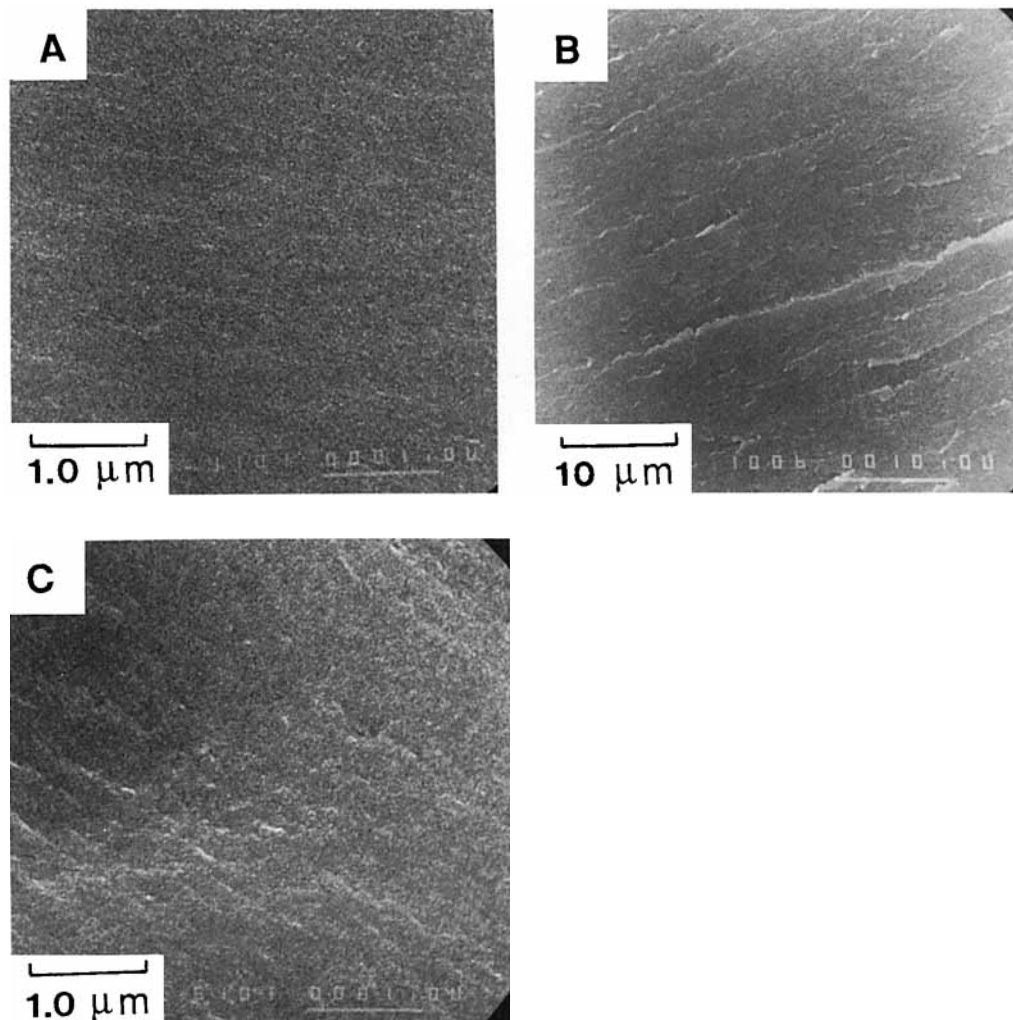
Figure 4 SEMs of fracture surfaces for the cured resins modified with 20 wt % of poly-
esters: (A) PBP (MW 7000); (B) PBP (MW 15,600); (C) PHP (MW 6300).

PBP, and PHP are 10.60, 12.42, 11.71, and 11.22, respectively (values calculated by Fedors' method[7]). The higher compatibility of polyesters such as PHP make their effectiveness as modifiers lower, as discussed later.

PBI was also effective as a modifier and comparable to PBP based on the fracture toughness and mechanical properties. The drawback is the poor compatibility of PBI with the uncured parent epoxy resin, compared with PBP: This makes processing harder. PHI was less effective than PBI on the basis of a larger expense of the mechanical properties. There is no distinction between o- and m-linkage in the calculation of the SP value; the SP values for PBP and PBI are the same. The order of the effectiveness of poly(alkylene isophthalate)s corresponds to that of poly(alkylene phthalate)s.

It is noteworthy that the carboxyl- or hydroxyl-terminated polyesters used in this study were chemically incorpolated into the epoxy matrix itself in the curing with acid anhydride such as MHHPA, and that the matrix was reinforced by the polyesters.

Two T_g's were observed in the modification with more than 20 wt % of poly(alkylene phthlate)s (Table IV). It is thought that the higher T_g's are based on the epoxy matrix and the lower ones on the polyesters, considering DSC results of the cured parent resin and the polyesters. The former T_g values were less than T_g for the unmodified resin, indicating that the polyesters dissolve partly into the epoxy matrix. The latter T_g's were higher than those of the polyesters themselves as shown in Table II. This would be perhaps due to the steric restriction of molecular motion of the polyesters, induced by chemical
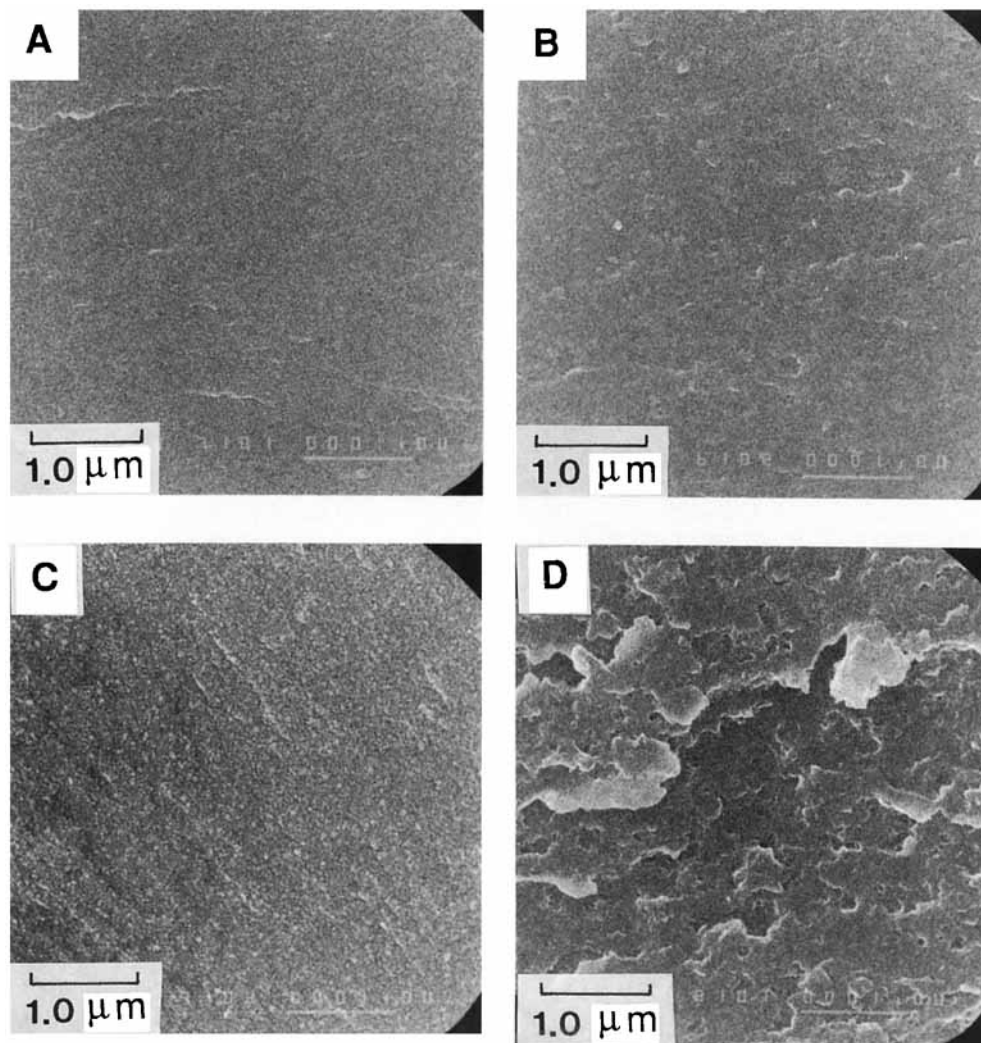
Figure 5 SEMs of fracture surfaces for the cured resins modified with 20 wt % of poly-esters: (A) PBI (MW 7000); (B) PBI (MW 12,500); (C) PHI (MW 6500); (D) PHI (MW 13,200).

bonding between terminal groups of the polyesters and the epoxy matrix and by intermixing with the matrix. These thermal behaviors show the presence of phase-separated structures in the cured resins: Such structures are observed in the PEP modification by SEMs. It is worth noting that the higher T_g value for the resin with modified with 20 wt % of PEP (MW 7200), the most suitable modifier in this study, is not so low, compared to T_g for the parent resin (Table III). This might be explained by both the molecular structure and MW of the used poly-esters: The T_g values for PEP-modified resins were higher than those for resins modified with other polyesters and the use of the higher MW PEP led to an increase in T_g.

The toughening mechanism can be explained in terms of the morphological and dynamic mechanical behaviors.

The fracture surfaces for the lower MW PEP modified resins were rough and ridgy, based on the plastic deformation of the epoxy matrix itself prior to failure, but no particle was observed. There were particles in the modification with PEP of MW more than 7200, but the volume fraction of particle was much smaller than the PEP concentration in the feed. This result indicates that PEP dissolves largely in the epoxy matrix phase. The fracture surface was rough in the modification with PBP, but no particle existed. The polyester was incorporated in the ma-trix owing to its good compatibility with the epoxy
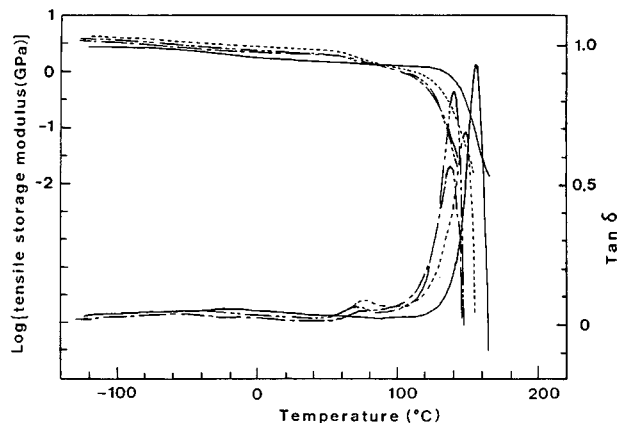
Figure 6 The effect of molecular weight of PEP on dynamic mechanical analysis for the cured resin containing of 20 wt % of the polyester: (———) control; (—·—) MW 6300; (—··—) MW 7200; (······) MW 10,100.

Figure 8 The effect of molecular weight of PBP on dynamic mechanical analysis for the cured resin containing of 20 wt % of the polyester: (———) control; (—·—) MW 4900; (—··—) MW 8700; (- - -) MW 15,600.

resin as shown by DMA results (Fig. 8). The fracture surfaces for the resin modified with other polyesters were similar to that for the PBP-modified cured system. The morphology of the cured resin shows that there is the high compatibility between the parent epoxy resin and the aromatic polyesters except for PEP. Such morphological behaviors correspond to the increase of the K_{IC}. The K_{IC} values for the resins modified with PEP of MW less than 6300 are lower than that for the PEP (MW 7200) modified resin having the microphase-separated structure (Table III). These results indicate that the presence of microphase separation is important for the toughening of the epoxy resin and that the increased compatibility leads to a decrease in the extent of microphase separation, which reduces the
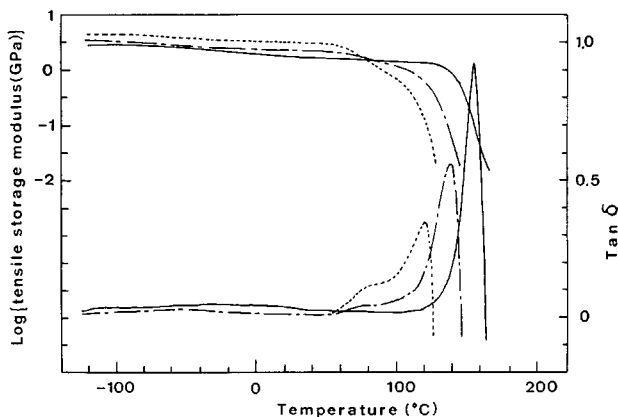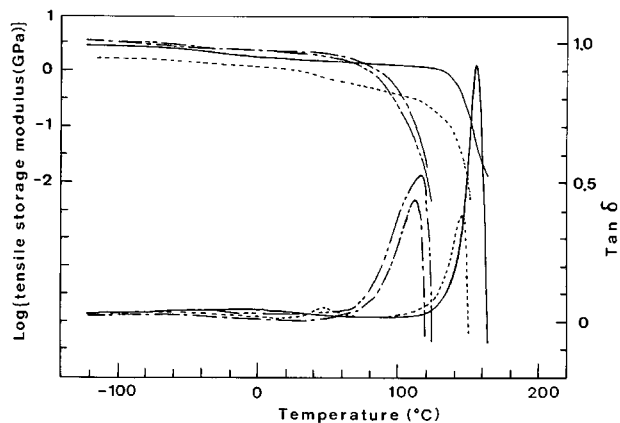
K_{IC} value as discussed below. The effectiveness of the polyesters as modifiers depends on their molecular structure and molecular weight. The use of the polyesters with higher MW led to macrophase-separation.

It is well known that the toughening of epoxy resins is based on the microphase-separated structure of the cured resin in the modification of epoxy resins with reactive elastomers[1,3]: The elastomer particles having a diameter of a few microns were dispersed in the epoxy matrix in the more effective modification system. The toughening mechanism can be explained by the fracture energy dissipation due to the delocalized plastic deformation around elastomer particles as stress concentrators. DMA results correspond to the morphologies of the cured
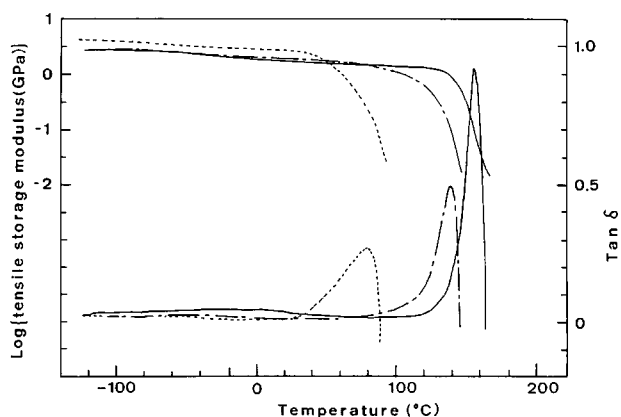

Figure 7 The effect of PEP concentration on dynamic mechanical analysis for the cured resin: (———) control; (—·—) 20 wt % addition; (- - -) 30 wt % addition.

Figure 9 The effect of PBP concentration on dynamic mechanical analysis for the cured resin: (———) control; (—·—) 10 wt % addition; (- - -) 30 wt % addition.

resins: the toughening of the cured epoxy resins can be correlated with the emergence of the new low temperature relaxation based on the inclusion of the reactive rubber. Such a correlation of relaxation height (or area) over the lower temperature range than T_g has been reported in the modification of the cured epoxy resin with reactive liquid rubbers.[8]

Terminally functionalized engineering thermoplastics are also effective as modifiers. For example, there are particles of diameter less than 1 μm in the epoxy matrix in the modification with amine-terminated polyether sulfone[2] and the toughening is thought to result from both the ductile yielding of the modifier particle and the delocalized plastic deformation initiated by the particle as a stress concentrator. Morphological behaviors show that the toughening mechanism in the PEP modification system might be similar to that in the polyether sulfone modification.

Dynamic mechanical behaviors of the PEP-modified resins correspond to morphologies of the resins. There is the shift towards lower temperature of the α-relaxation and the emergence of the α'-relaxation around 70°C in the modification with PEP. The α'-relaxation peak can be attributed to PEP segments restricted by the epoxy matrix. The molecular weight dependence of the tan δ curves (Fig. 6) shows that the compatibility of the parent resin with PEP reduces gradually with increasing the PEP molecular weight. The presence of particle dispersed in the epoxy matrix is observed morphologically in the use of PEP with MW more than 7200 (Fig. 3). No particle is observed in the modification with PEP of MW 6300, but dynamic mechanical behaviors shows that the microphase-separated structure exists to a less extent: This fact is also shown in its DSC result (Table IV). It is interesting that there is an increase in tensile storage modulus over the temperature range lower than T_g, compared to the parent resin. This indicates that the epoxy resin is reinforced by PEP dissolved into the matrix. The increased tensile storage modulus corresponds to the increased Young's modulus in tensile tests. Dynamic mechanical behaviors in the modification with PEP of MW 6300 are interesting and important (Fig. 7). The increased PEP concentration resulted in the lower temperature shift of the α-relaxation peak position and its more broadening, and the emergence of the α'-relaxation peak. The K_{IC} values for the PEP (MW 6300) modified resin increase linearly with an increase in the PEP concentration (Fig. 2). In the modification with PEP the broadness of the α-relaxation and the emergence of the α'-relaxation can explain the toughening of the modified resin system

(Fig. 6). Such a correlation of dynamic mechanical behaviors with the toughness of cured resins has been reported for the modification of epoxy resins with carboxyl terminated butadiene acrylonitrile rubber (CTBN)[1] or reactive acrylic elastomers.[3]

In the modification system with PBP of MW less than 8700 the α-relaxation peaks of the tan δ curves become broader and their peak positions shift towards lower temperatures without the emergence of a new relaxation peak (Fig. 8). These dynamic mechanical behaviors indicate that PBP has higher compatibility with the epoxy resin than PEP as discussed above. The use of higher MW PBP (15,600) led to the narrowness and the shift towards higher temperature of the α-relaxation, and the emergence of the α'-relaxation peak. This result shows the presence of phase-separation structure and corresponds to the morphology of the modified resin [Fig. 4(b)]. This modified resin whitened in tensile tests perhaps owing to macrophase separation. When the PBP (MW 7000) concentration increases up to 30 wt %, the α-relaxation peak becomes broader gradually and its peak position shifts towards lower temperature, compared to the parent resin, but the α'-relaxation peak is not observed (Fig. 9). The gradual broadness of the α-relaxation peak can be correlated with the linear increase of the K_{IC} values with the increased PBP concentration (Fig. 2). These behaviors also show the high compatibility of PBP and the parent resin. Dynamic mechanical behaviors in the PBP (MW 7000) modification are different from those in the modification with PEP (MW 6300) (Fig. 7). Such a difference would be based on that in their compatibility with the epoxy resin system.

The morphological and dynamic mechanical behaviors of the PEP-modified resin indicate that the microphase separation is important to reduce the brittleness of the epoxy resin, where the delocalized plastic deformation around particles dissipates the fracture energy. DSC results for the resins modified with other polyesters suggest the presence of microphase-separated structures, which are not observed by SEMs. Then the contribution of such a microphase-separated structure to the toughening of the epoxy resin is far smaller in these systems than in the PEP modified system. It is noteworthy that PBP is a more effective modifier, though no particle is observed by SEM. The increased K_{IC} value in the PBP modification suggests that the toughening of the epoxy matrix itself would be also important to improve the toughness of the epoxy resin.

In conclusion, the aromatic polyesters are highly effective as modifiers for the epoxy resin. The com-

bination of (iso)phthalic acids with α,ω-alkanediols enable us to prepare desired modifiers. The more effective modifiers are PEP, PBP, and PBI of moderate MW. The modification with both PEP (MW less than 7200) and PBP (MW less than 7000) led to an increase in the fracture toughness of the cured resin at no expense of its mechanical properties. The most suitable compositions for the modification was inclusion of 20 wt % of PEP (MW 7200), which resulted in a 150% increase in the fracture toughness K_{IC} at no expense of its mechanical properties, though its thermostability is a little lower, compared to the parent resin. The use of the polyesters with higher MW led to the decreased mechanical properties of the cured resins owing to the macrophase separation. The improved toughness of the resin modified with the more effective polyester, PEP, would be partly due to the dissipation of the fracture energy by blunting the crack tip based on the delocalized plastic deformation and partly due to the reinforcement of the epoxy matrix itself by the incorporated polyester. The latter would be also more important for the toughening of the epoxy resin with the polyesters except for PEP.

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