

# Toughening of Aromatic Diamine-Cured Epoxy Resins by Poly(butylene phthalate)s and the Related Copolyesters

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## SYNOPSIS

Aromatic polyesters, prepared by the reaction of aromatic dicarboxylic acids and 1,4-butanediol, were used to improve the toughness of bisphenol-A diglycidyl ether epoxy resin cured with *p,p'*-diaminodiphenyl sulfone. These polyesters contained poly(butylene phthalate)s (PBP), poly(butylene phthalate-*co*-butylene isophthalate)s, poly(butylene phthalate-*co*-butylene terephthalate)s, and poly(butylene phthalate-*co*-butylene 2,6-naphthalene dicarboxylate)s. All aromatic polyesters used in this study were soluble in the epoxy resin without solvents and were found to be effective as modifiers for toughening the cured epoxy resin. For example, the inclusion of 20 wt % PBP (MW 16,300) led to a 120% increase in the fracture toughness ( $K_{IC}$ ) of the cured resin with no loss of mechanical and thermal properties. The toughening mechanism was discussed in terms of the morphological and dynamic viscoelastic behaviors of the modified epoxy resin system. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Epoxy resins are one of the most important 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 with reactive liquid rubbers such as carboxyl-terminated butadiene acrylonitrile rubbers<sup>1</sup> or terminally functionalized engineering thermoplastics.<sup>2,3</sup> In previous papers, various kinds of epoxide-containing acrylic elastomers have been reported as improving the toughness of *p,p'*-diaminodiphenyl sulfone (DDS)-cured epoxy resins, where vinylbenzyl glycidyl ether and glycidyl (meth)acrylate were used as epoxy-containing monomers.<sup>4-8</sup>

Engineering thermoplastics are interesting materials as modifiers for epoxy resins from the

viewpoint of the maintenance of mechanical and thermal properties for the matrix resins. Modification of epoxy resins with various types of ductile thermoplastics have been studied as alternatives to reactive rubbers for improving the toughness of epoxy resins. Various kinds of engineering thermoplastics have been examined as modifiers, where commercial poly(ether sulfone)s,<sup>9-11</sup> functionalized polysulfones,<sup>2,12,13</sup> poly(etherimide)s,<sup>3,14-16</sup> poly(aryl ether ketone)s,<sup>17,18</sup> and poly(phenylene oxide)<sup>19</sup> were reported as effective modifiers. We found that *N*-phenylmaleimide-styrene copolymers and *N*-phenylmaleimide-*N*-cyclohexylmaleimide-styrene terpolymers were effective modifiers for diglycidyl ether of bisphenol-A (DGEBA).<sup>20-24</sup>

In a previous paper,<sup>25</sup> we reported that aromatic polyesters, prepared by the reaction of (iso)phthalic acids and  $\alpha,\omega$ -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. Most recently, poly(ethylene phthalate)s (PEP) and the related co-

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polyesters have been reported as effective modifiers for highly cross-linked epoxies.<sup>26</sup>

In the modification of epoxies with PEP, the toughening could be achieved with no loss of mechanical properties because of particulate structures of the modified resins. We report the modification of DDS-cured DGEBA resins with poly(butylene phthalate)s (PBP) and related copolyesters. The effects of structure, molecular weight, and amount of polyesters used on the toughness of the cured resin were examined.

## EXPERIMENTAL

### Materials

The epoxy resin was the liquid DGEBA (Epikote 828, Shell Chemical Industrial Co., epoxy equivalent weight 190). DDS was used as a curing agent. The aromatic polyesters were prepared by the reaction of 1,4-butanediol and aromatic dicarboxylic acids or their derivatives as reported previously.<sup>25</sup> Aromatic dicarboxylic acid and the derivatives contained

**Table I** Characterization of Aromatic Polyesters

Entry No.	Polyester <sup>a</sup> Composition	$M_{GPC}^b$ ( $10^3$ )	$M_n^b$ ( $10^3$ )	$M_w/M_n$	$T_g^c$ (°C)	Acid Content (mEq/g)
<b>PBP</b>						
3	—	4.2	3.8	1.4	-10	0.080
1	—	8.2	5.0	2.0	-9	—
4	—	11.4	6.6	2.0	-2	0.098
2	—	16.3	10.7	1.8	-5	—
5	—	28.1	19.7	1.7	1	—
<b>PBPI</b>						
7	IP 10	6.8	4.7	1.8	—	—
3	10	10.9	7.8	1.7	-14	—
2	10	15.8	10.3	1.8	—	—
1	10	21.7	13.8	1.8	-10	—
8	20	7.1	5.4	1.6	—	—
5	20	10.7	6.1	2.0	-13	—
6	20	15.7	10.2	1.8	—	—
4	20	24.3	15.6	1.8	-9	—
9	50	18.2	12.1	1.8	—	—
<b>PBPT</b>						
9	TP 10	11.7	7.5	1.7	—	—
10	20	12.5	7.8	1.8	-6	—
1	50	6.5	4.8	1.7	2	—
3	50	7.3	5.8	1.6	3	0.025
2	50	9.9	7.0	1.7	5	—
4	50	13.2	7.2	2.1	7	0.019
7	50	15.6	9.5	1.9	8	0.021
8	50	23.3	13.0	2.0	11	0.011
<b>PBPN</b>						
10	ND 10	10.6	6.9	1.7	—	—
8	10	17.0	11.0	1.8	—	—
3	20	6.5	4.0	1.9	—	—
5	20	11.0	7.1	1.8	—	—
2	20	14.5	9.9	1.7	8	—
9	20	18.0	11.0	1.8	—	—
6	20	22.2	14.4	1.8	—	—
7	20	30.5	19.1	1.8	11	—
12	50	10.6	6.8	1.8	—	—
11	54	13.0	7.8	1.8	23	—

<sup>a</sup> IP, isophthalate unit; TP, terephthalate unit; ND, 2,6-naphthalene dicarboxylate unit mol %.

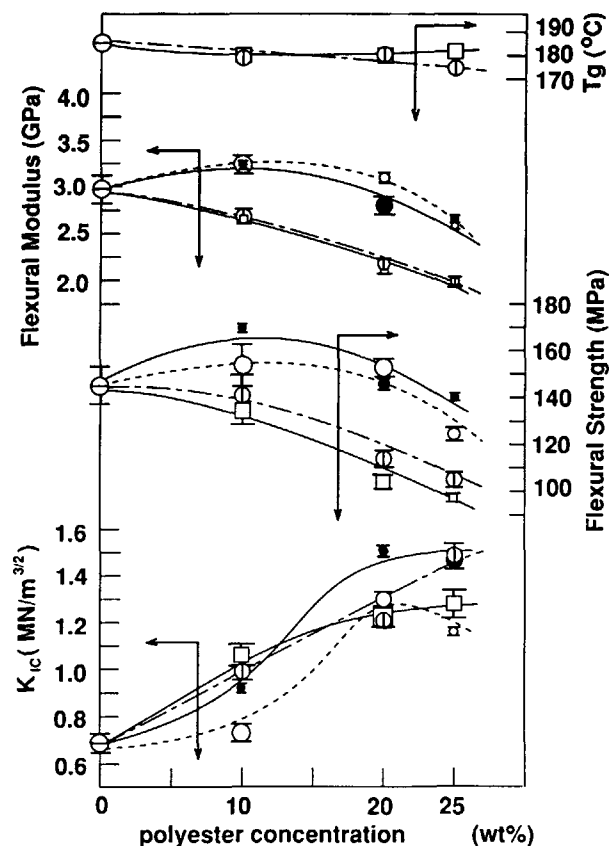
<sup>b</sup> By GPC.

<sup>c</sup> By DSC.

Table II Physical Properties of Modified Epoxy Resins

Entry No.	Polyester <sup>a</sup>				Flexural Properties				$T_g$	
	No. <sup>b</sup>	Composition (mol %)	MW ( $10^3$ )	$K_{IC}^c$ (MN/m <sup>3/2</sup> )	Specimens Tested	Strength <sup>c</sup> (MPa)	Modulus <sup>c</sup> (GPa)	Specimens Tested	DSC (°C)	DVA <sup>d</sup> (°C)
Control			—	0.69 ± 0.04	16	145 ± 8	2.98 ± 0.15	14	185	203
PBP series										
B19	PBP2	—	16.3	1.51 ± 0.02	7	146 ± 3	2.80 ± 0.09	6	— <sup>e</sup>	200
02	PBP5	—	28.1	1.43 ± 0.01	7	122 ± 4	2.32 ± 0.09	6	177	—
PBPI series										
BI02	PBPI2	IP 10	15.8	1.28 ± 0.04	6	120 ± 2	2.32 ± 0.03	8	173	—
01	PBPI1	10	21.7	1.33 ± 0.05	8	109 ± 3	2.17 ± 0.04	8	185	—
06	PBPI6	20	15.7	1.32 ± 0.03	8	132 ± 3	2.67 ± 0.05	8	—	—
10	PBPI9	50	18.2	1.34 ± 0.05	6	125 ± 2	2.46 ± 0.04	6	175	—
PBPT series										
BT10	PBPT9	TP 10	11.7	1.30 ± 0.03	9	153 ± 4	3.11 ± 0.04	7	— <sup>e</sup>	—
11	PBPT10	20	12.5	1.26 ± 0.07	8	147 ± 10	3.05 ± 0.05	7	— <sup>e</sup>	—
06	PBPT7	50	15.6	1.23 ± 0.05	6	104 ± 3	2.11 ± 0.03	7	179	207
07	PBPT8	50	23.3	1.19 ± 0.03	9	103 ± 1	2.03 ± 0.03	8	184	—
PBPN series										
EN07	PBPN8	ND 10	17.0	1.24 ± 0.05	5	142 ± 5	2.70 ± 0.13	5	— <sup>e</sup>	—
12	PBPN9	20	18.0	1.30 ± 0.04	7	139 ± 2	2.70 ± 0.04	6	— <sup>e</sup>	—
14	PBPN12	50	10.6	1.13 ± 0.02	6	134 ± 6	2.71 ± 0.15	6	— <sup>e</sup>	—
13	PBPN11	50	13.1	1.07 ± 0.02	5	115 ± 2	2.33 ± 0.07	5	185	—

<sup>a</sup> Polyester content 20 wt %.<sup>b</sup> Entry number in Table I.<sup>c</sup> Values are means ± SD.<sup>d</sup> By dynamic viscoelastic analysis.<sup>e</sup> Not obtained by DSC.



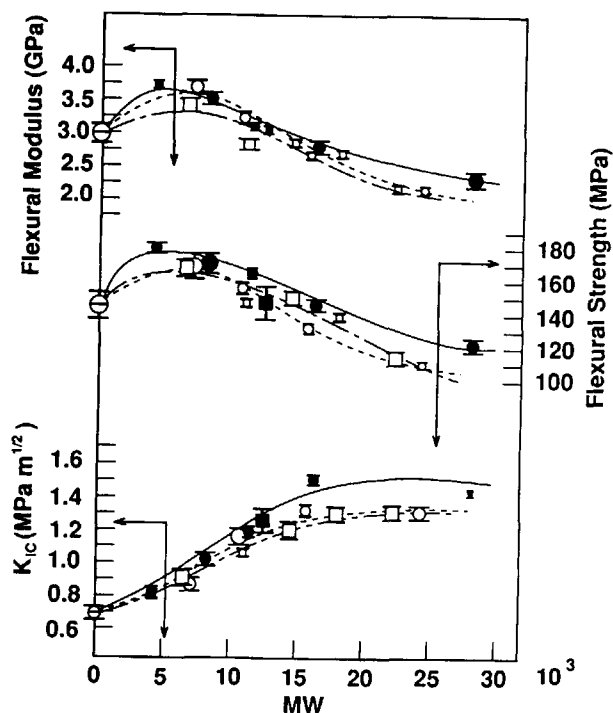
**Figure 1** Physical properties of the modified resins as function of polyesters concentration.  $\ominus$ , Control;  $\bullet$ , PBP (MW 16,300);  $\circ$ , PBPT (10 mol % TP unit, MW 11,700);  $\square$ , PBPT (50 mol % TP unit, MW 15,600);  $\odot$ , PBPN (20 mol % ND unit, MW 22,200).

phthalic anhydride, isophthalic acid, dimethyl terephthalate, and dimethyl 2,6-naphthalene dicarboxylate (provided by Mitsubishi Gas Chemical Corp.). Other reagents were used as received.

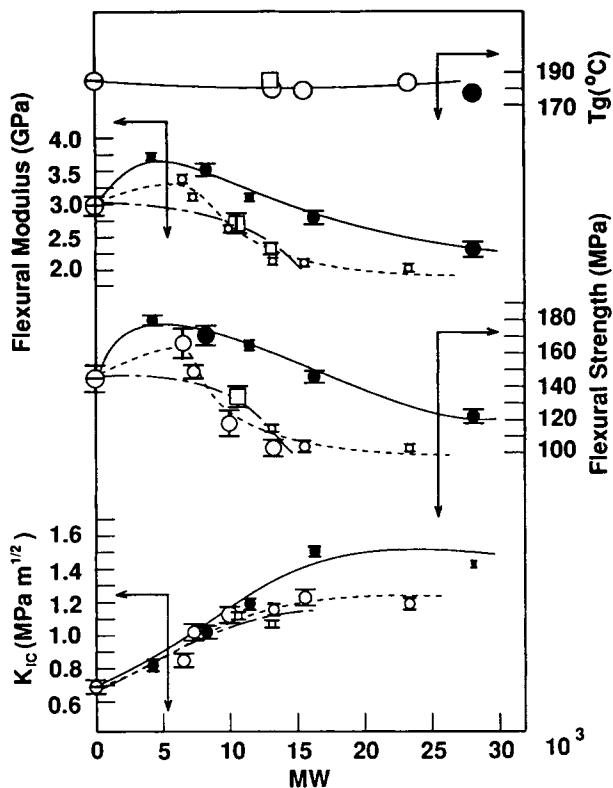
#### Measurements

$^1\text{H-NMR}$  spectra were recorded on a 90-MHz instrument (JEOL JNM-9MX 90) using  $\text{CDCl}_3$  as solvent and tetramethylsilane as internal standard. Molecular weights of polyesters were determined by gel permeation chromatography (Shimadzu LC-5A instrument) 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 au-

tograph 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  $K_{\text{IC}}$  was measured in a three-point bent geometry at a cross head speed of 1 mm/min (ASTM E-399). The glass transition temperatures  $T_g$ s of both polyesters and cured resins were measured as the onset temperatures by differential scanning calorimetry (DSC) (Shimadzu DSC 41M type) at a heating speed of  $10^\circ\text{C}/\text{min}$ . Scanning electron micrographs (SEM) were taken with a JEOL JSM 35 or a Hitachi SEM S-2100A instrument using failed specimens in the  $K_{\text{IC}}$  tests. For the modified resin invisible to the above conventional SEMs, ion etching of the polished surface was carried out by Hitachi flat milling E-3200 instrument (applied voltage 5 kV, charge current 1 mA, milling time 40 min, ion incident angle  $60^\circ$ ), and a high-resolution SEM with a field emission gun (Hitachi FE-SEM, S-4500 type) was used. Dynamic viscoelastic analysis was performed with a Rheometrics RDS-II type (Rheometrics Co.) between  $-150$  and  $250^\circ\text{C}$  at a heating speed of  $5^\circ\text{C}/\text{min}$  at frequency of 1 Hz.



**Figure 2** Dependence of physical properties for the modified resins on polyester molecular weight; 20 wt % modifier addition.  $\ominus$ , Control;  $\bullet$ , PBP;  $\circ$ , PBPI (20 mol % IP unit);  $\blacksquare$ , PBPT (20 mol % TP unit);  $\square$ , PBPN (20 mol % ND unit).



**Figure 3** Dependence of physical properties for the modified resins on solid polyester molecular weight; 20 wt % modifier addition.  $\ominus$ , Control;  $\bullet$ , PBP;  $\circ$ , PBPT (50 mol % TP unit);  $\square$ , PBPN (50 mol % ND unit).

### Curing Procedure

The aromatic polyester was dissolved into the epoxy resin without solvents by heating at 160°C. Then the curing agent, DDS, was added to the mixture, which was kept at 120°C for about 1 h to dissolve DDS. The resulting clean mixture was poured into a silicone rubber mold preheated at 120°C. The curing cycle was 1 h at 120°C and 5 h at 180°C. DDS was used stoichiometrically to the epoxy resin. The amount (wt %) of the aromatic polyester used was based on the epoxy resin matrix (DGEBA + DDS).

## RESULTS

### Characterization of the Aromatic Polyesters

In this study, various kinds of aromatic polyesters were prepared in quantitative yield by polycondensation of 1,4-butanediol and aromatic dicarboxylic acid or the derivatives and used as modifiers, which

contain PBP, poly(butylene phthalate-*co*-butylene isophthalate)s (PBPI), poly(butylene phthalate-*co*-butylene terephthalate)s (PBPT), and poly(butylene phthalate-*co*-butylene 2,6-naphthalene dicarboxylate)s (PBPN). The polyester compositions were equal to the feed compositions by <sup>1</sup>H-NMR spectroscopy. Table I reports some characteristic properties of the aromatic polyesters. The gel permeation chromatography-average molecular weight ( $M_{GPC}$ ) was used as a measure of the molecular weight (MW) here and in previous articles,<sup>25,26</sup> because the number-average molecular weight is highly sensitive to the presence of a small amount of lower-molecular-weight materials. The  $T_g$  of the aromatic polyesters had the tendency to increase with decreasing the phthalic acid unit content. It is noteworthy that the polyesters containing 50 mol % terephthalate (TP) or 2,6-naphthalene dicarboxylate (ND) units became solid, compared with the other viscous liquid materials.

### Mechanical and Thermal Properties of Modified Epoxy Resins

The cured parent epoxy resin was transparent, but the modified resins went from transparent to opaque during curing, depending on polyester structure and concentration. Table II shows the representative results for the modification of the epoxy resin. Figure 1 shows the mechanical and thermal properties of the modified resins as a function of concentration of polyesters. The fracture results indicate that the use of 20 wt % polyester is essential to reduce the brittleness of epoxies.

When using PBP (MW 16,300) and PBPT (10 mol % TP unit, MW 11,700) as modifiers, the flexural strength and modulus for the modified resins were maintained, compared with those for the unmodified epoxy resin. The modified resins were transparent, and DSC analysis did not show the endothermic behavior based on  $T_g$ , so their  $T_g$  values were measured by dynamic viscoelastic analysis as shown later.  $T_g$  for the PBP-modified resin was equal to that for the unmodified resin (Table II, B19).

In the modification with both PBPT (50 mol % TP unit, MW 15,600) and PBPN (20 mol % ND unit, MW 22,200), the flexural properties of the modified resins decreased with increasing polyester concentration, compared with those for the parent epoxy resin. The PBPT-modified resins were transparent and the PBPN-modified resins opaque, where the  $T_g$  could be determined by DSC (Fig. 1). The  $T_g$  for the PBPT (50 mol % TP unit)-modified resins

**Table III Morphological Results**

Entry No.	Polyester		Resin Composition		$D^a$ ( $\mu\text{m}$ )	$V_f^b$	No. Particles/100 $\mu\text{m}^2$ ( $10^2$ )
	Composition	MW	Matrix/Polyester				
Control	—	—	100/0		—	—	—
PBP series							
B19	—	16,300	80/20		— <sup>c</sup>	—	—
B02	—	28,100	80/20		$0.25 \pm 0.06$	0.166	3.1
PBPI series							
BI01	IP 10	21,700	80/20		$0.18 \pm 0.07$	0.111	4.0
BI04	20	24,300	80/20		$0.14 \pm 0.05$	0.149	8.5
BI10	50	18,000	80/20		$0.12 \pm 0.04$	0.112	8.8
PBPT series							
BT04	TP 50	13,200	80/20		$0.24 \pm 0.08$	0.220	4.7
BT08	50	15,600	90/10		$0.14 \pm 0.05$	0.064	3.7
BT06	50	15,600	80/20		$0.31 \pm 0.06$	0.190	2.4
BT09	50	15,600	75/25		$0.89 \pm 0.33$	0.421	0.6
PBPN series							
EN04	ND 20	22,000	80/20		$0.17 \pm 0.06$	0.127	5.0
EN13	50	10,600	80/20		$0.17 \pm 0.07$	0.137	5.5
EN14	50	13,100	80/20		$0.48 \pm 0.14$	0.277	1.4

<sup>a</sup> Average particle diameter; values are means  $\pm$  SD.

<sup>b</sup> Volume fraction of dispersed particles.

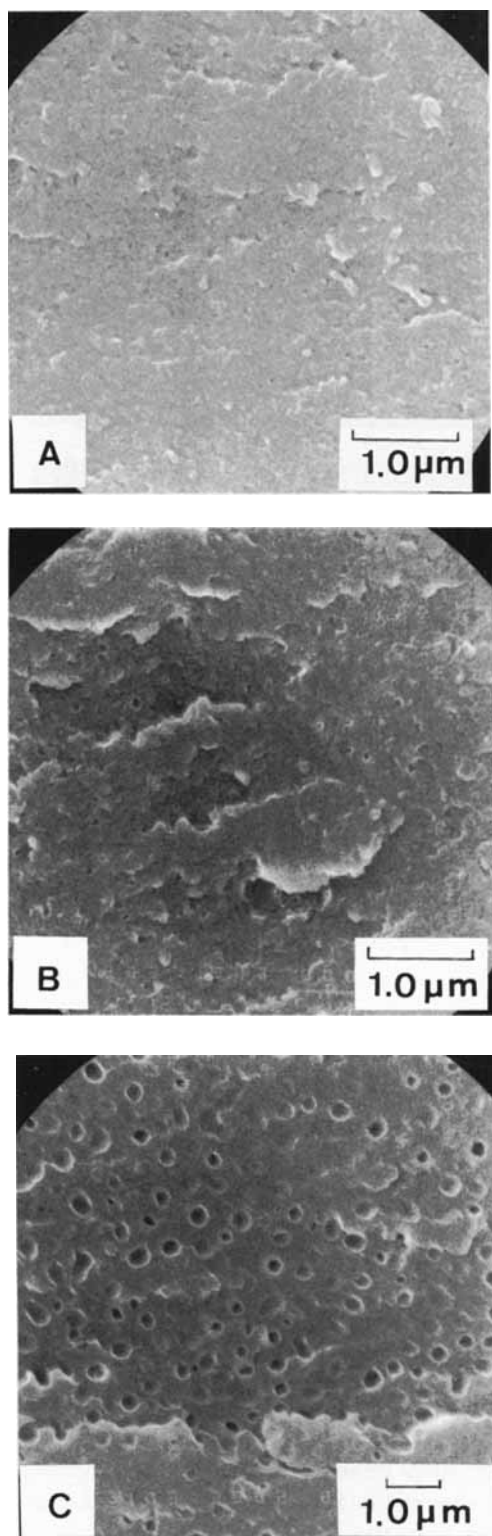
<sup>c</sup> Ill-defined particles with diameter of less than ca. 50  $\mu\text{m}$ .

were equal or slightly lower than that for the parent resin.

Figure 2 shows the dependence of the mechanical and thermal properties for the modified resins on polyester MW on 20 wt % addition of viscous liquid polyester. The  $K_{IC}$  for the modified resin increased with increasing polyester MW and leveled off. The optimum MW of the polyesters was about 15,000, where  $K_{IC}$  increased 70–120% depending the polyester structure.  $K_{IC}$  for the PBP (MW 16,300)-modified resin increased 120% at no deterioration of flexural and thermal properties. When using higher MW (28,100) PBP, flexural and thermal properties of the modified resin deteriorated (Table II; B02). The use of PBPI (20 mol % isophthalate (IP) unit, MW 15,700) led to a 90% increase in  $K_{IC}$  at a slight expense of flexural strength and modulus;  $T_g$  for the transparent PBPI-modified resin could not be obtained by DSC (Table II, BI06). The efficiency of PBPI as a modifier was rather insensitive to PBPI structure (Table II, BI02, 06, and 10). PBPI (10, 20, or 50 mol % IP units), PBPT (10 or 20 mol % TP units), and PBPN (10 or 20 mol % ND units) were slightly less effective than PBP. When using PBPT (20 mol % TP unit, MW 12,500) and PBPN (20 mol % ND unit, MW < 18,000), the modified resins

were transparent and the  $T_g$  could not be determined by DSC.

PBPT (50 mol % TP unit) and PBPN (50 mol % ND unit) were solid and interesting materials in terms of good processability. In the modification with PBPT (50 mol % TP unit), the dependence of physical properties of the cured resins on PBPT content is shown in Figure 1. Figure 3 shows the dependence of the mechanical and thermal properties for the modified resins on MW of solid polyesters (50 mol % TP or ND units) on 20 wt % addition. The  $K_{IC}$  value increased with increasing polyesters MW. The use of PBPT (MW 15,600) led to 80% increase in  $K_{IC}$  at a loss of flexural properties. When using PBPN (MW 10,600),  $K_{IC}$  increased 60% at no expense of flexural strength. PBPT (50 mol % TP unit) and PBPN (50 mol % ND unit) were less effective modifiers for epoxies than PBP, but the PBPN-modified resins had balanced properties, considering their good processabilities. When using PBPT of MW < 7300, the modified resins were transparent and their  $T_g$  could not be measured by DSC. The opaque resins showed the endothermic behavior by DSC.  $T_g$ s for the modified resins were equal or slightly lower than that for the parent resin. In general, DSC



**Figure 4** SEMs of fracture surfaces for PBP-modified resins. (A) 20 wt % addition of PBP (MW 16,500), magnification  $\times 20,000$ ; (B) 25 wt % addition of PBP (MW 16,500), magnification  $\times 20,000$ ; (C) 20 wt % addition of PBP (MW 28,100), magnification  $\times 10,000$ .

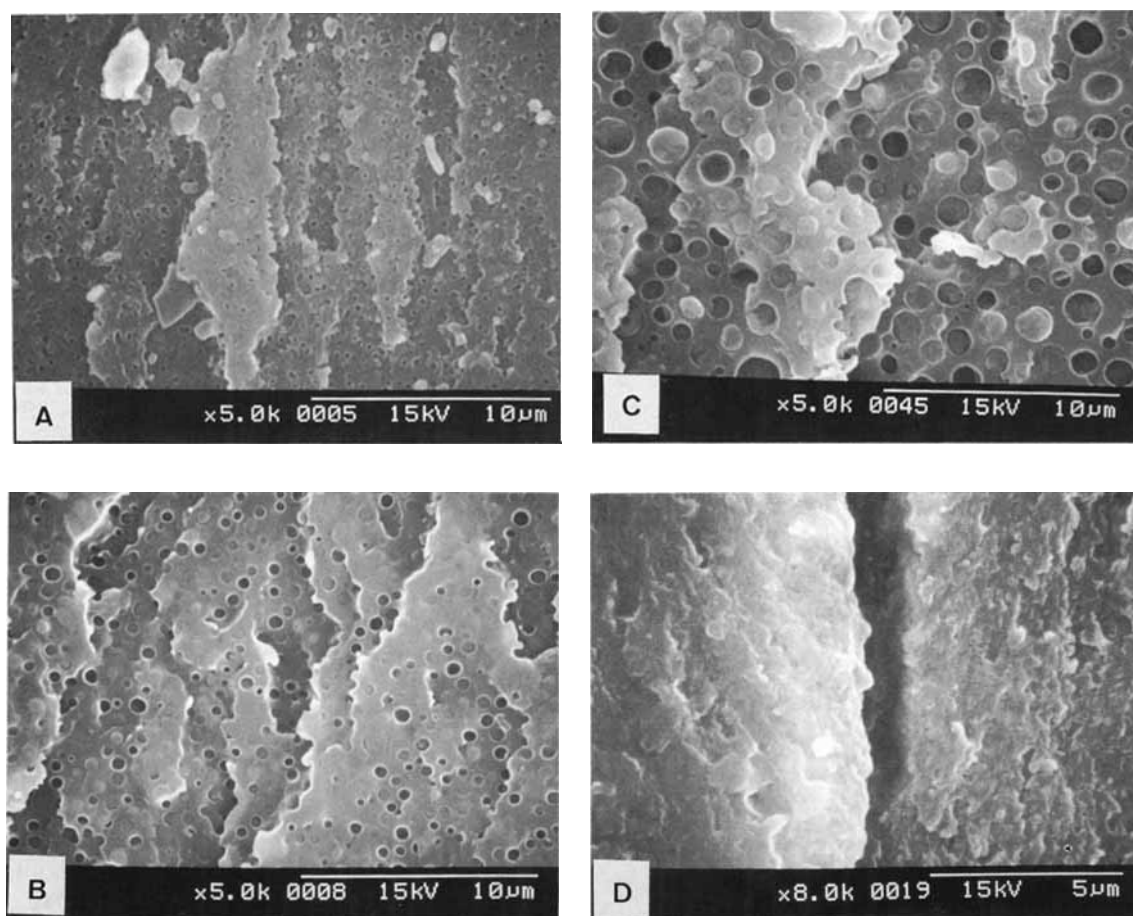
was not useful to measure the  $T_g$  for the transparent modified resins in this study.

### Morphologies of the Modified Epoxy Resins

The morphologies of the cured resins were investigated by SEM. The parent epoxy resins had only one phase as reported previously.<sup>4</sup> When using 20 wt % of some kinds of the polyesters, the modified resins were transparent and the phase-separated structure could not be observed by SEM; such polyesters contain PBP (MW  $< 16,300$ ), PBPI (10 mol % IP unit, MW  $< 15,800$ ), PBPI (20 mol % IP unit, MW  $< 15,700$ ), PBPT (10 mol % TP unit, MW 11,700), PBPT (20 mol % TP unit, MW 12,500), PBPT (50 mol % TP unit, MW  $< 7300$ ), PBPN (10 mol % ND unit), and PBPN (20 mol % ND unit, MW  $< 18,000$ ) (Table I). When using the other polyesters, two-phase morphologies with polyester-rich spherical particles dispersed in the epoxy-rich matrix could be observed by conventional SEM. The morphological results are collected in Table III.

Figure 4 shows SEM micrographs for the PBP-modified resins. When using 20 or 25 wt % of PBP (MW 16,300), a very small amount of fine particles was observed, but SEM micrographs were obscure even under a high magnification ( $\times 20,000$ ) [Fig. 4(A) and (B)]. In the modification with PBP (MW 28,100), the modified resin has a particulate morphology, and some particles coagulate each other [Fig. 4(C)].

An example of the PBPI-modified resins is shown in Figure 5(A). The PBPI-modified resins had similar morphologies independent of the modifier structure, and their volume fraction  $V_f$  was smaller than the feed compositions (Table III, BI01, 04, and 10). This indicates high compatibility of PBPI with the epoxy matrix. The PBPT (50 mol % TP unit, MW 15,600)-modified resins had particulate morphologies [Fig. 5(B) and (C)]. The average diameter  $D$  of dispersed particles increased with increasing PBPT content. Although the lower MW PBPN (20 mol % ND unit, MW 18,000)-modified resins did not show a phase-separated structure on 20 wt % addition, the modified resin became translucent on 25 wt % addition of the same modifier and smaller amounts of particles were observed [Fig. 5(D)]. The opaque PBPN (20 mol % ND unit, MW 22,000)-modified resins had particulate morphologies, and the average diameter of dispersed particles increased with increasing PBPN content [Fig. 5(E) and (F)]; the characteristics of the PBPN (25 wt %)-modified resin was irregular PBPN-rich particles, where more amounts of particles coagulated each other [Fig.



**Figure 5** SEMs of fracture surfaces for the modified resins. (A) 20 wt % addition of PBPI (10 mol % IP unit, MW 21,700); (B) 20 wt % addition of PBPT (50 mol % TP unit, MW 15,600); (C) 25 wt % of PBPT (50 mol % TP unit, MW 15,600); (D) 25 wt % of PBPN (20 mol % ND unit, MW 18,000); (E) 20 wt % of PBPN (20 mol % ND unit, MW 22,000); (F) 25 wt % of PBPN (20 mol % ND unit, MW 22,000); (G) 20 wt% of PBPN (50 mol% ND unit, MW 10,600); (H) 20 wt% of PBPN (50 mol% ND unit, MW 13,100).

5(F)], compared with the morphologies of the other polyesters-modified resins [Fig. 5(C)].

PBP was a most effective modifier in this study, but the morphology of the lower MW PBP-modified resins could not be observed by conventional SEM. The SEMs of the lower MW PBP-modified resin etched by  $\text{CHCl}_3$  (3 days) were also obscure (not indicated here). In the present modification, transmission electron microscopy was not useful, because the aromatic polyesters used here cannot be stained selectively by  $\text{OsO}_4$  or  $\text{RuO}_4$ . Then, ion etching of the polished surface by  $\text{Ar}^+$  plasma was tried for the cured resin modified with 20 wt % of PBP (MW 16,300), the most effective modification system. Figure 6 shows micrographs of ion-etched specimens taken by high-resolution SEM with a field emission gun. The SEM micrograph for the unmodified resin

was featureless [Fig. 6(A)]. For the micrograph of the PBP-modified resin, well-dispersed particles with diameter  $< 60$  nm were observed [Fig. 6(B)]. At present, the ion-etching technique is under progress, and it is unknown which component, the matrix or the modifier, will be etched out by bombarding with  $\text{Ar}^+$ . It is thought that the particles in Figure 6(B) would be PBP-rich materials, considering the ion-etching result of the unmodified resin and the morphological results in Figure 4(A). The result indicates that the use of conventional SEM is unsuitable to analyze the microstructure of the transparent modified resins, but FE-SEM is useful. In the present modification, some of the transparent modified resins would also have nanometer-order particles dispersed in the matrix, considering the following dynamic viscoelastic behaviors.



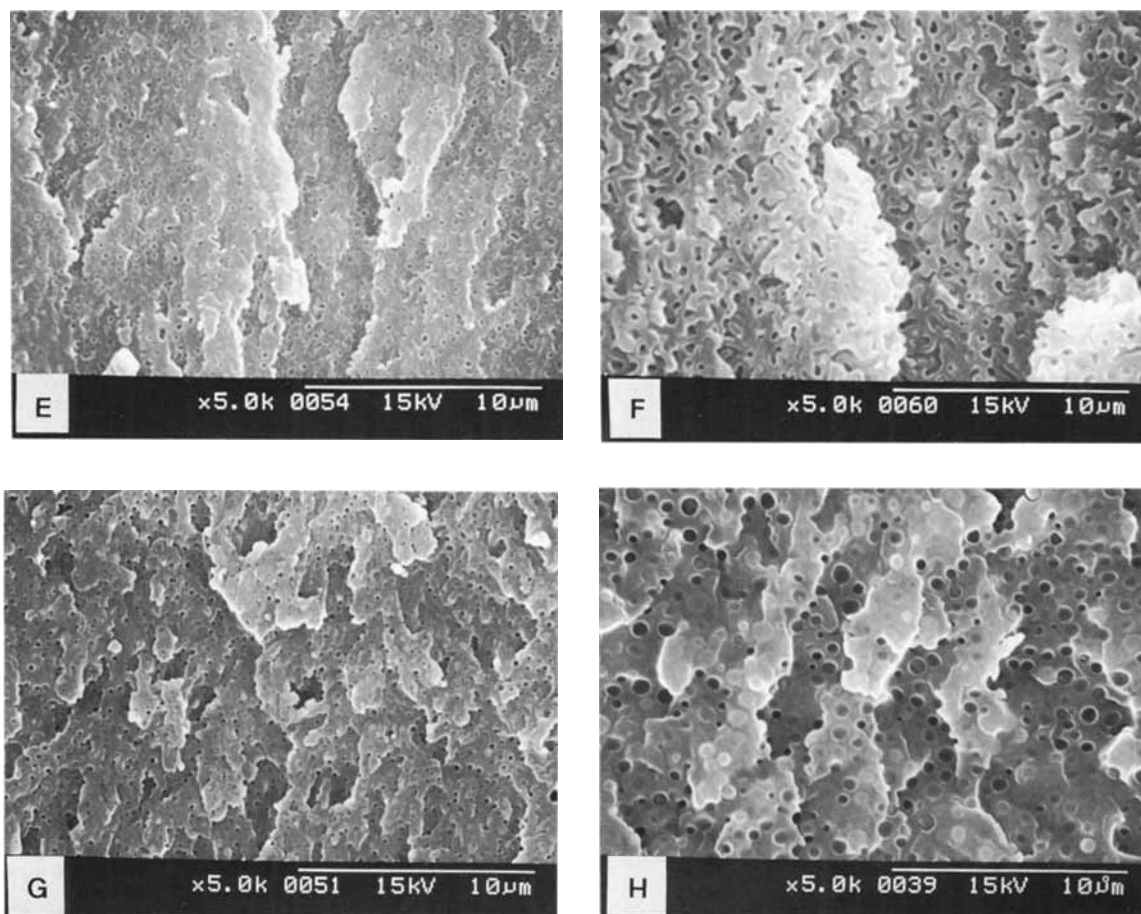


Figure 5 (Continued from the previous page)

### Dynamic Viscoelastic Analysis of Modified Epoxy Resins

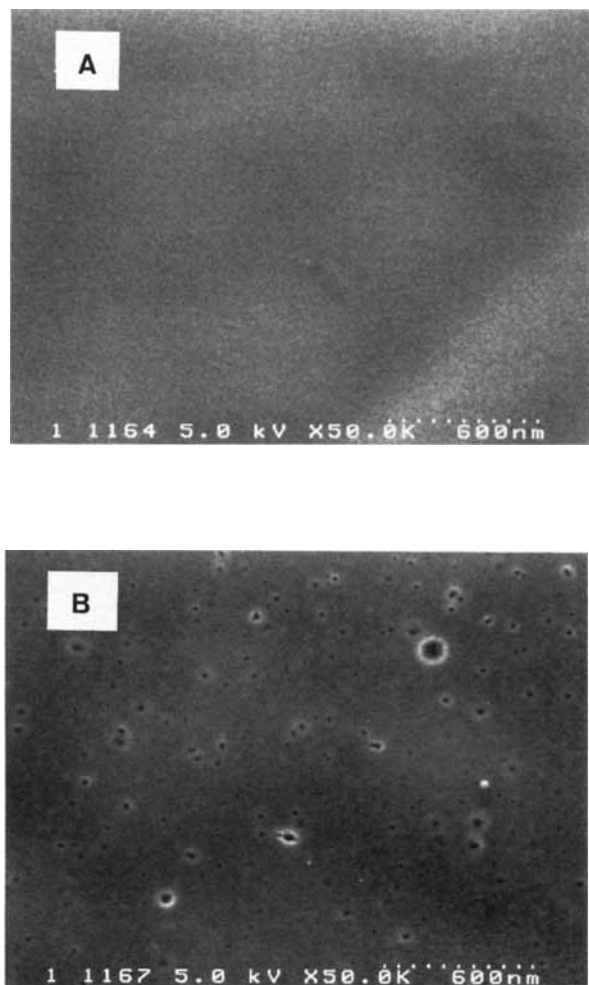
Figure 7 shows the storage modulus  $G'$  and  $\tan \delta$  curves for the unmodified and PBP-modified resins. In the modification with 10 wt % of PBP (MW 16,300), the peak position of the  $\alpha$ -relaxation in the  $\tan \delta$  curve shifted toward lower temperature, and its shape became broader, compared with that for the unmodified resin. When using 20 wt % of PBP (MW 16,300), the broadness of the  $\alpha$ -relaxation peak became greater and a new relaxation ( $\alpha'$ -relaxation) peak appeared at 14°C. The existence of the  $\alpha'$ -relaxation peak indicates the existence of a phase-separated structure, which corresponds to the morphological result [Fig. 6(B)]. The storage moduli at room temperature were larger than that for the unmodified resin.

In the modification with 20 wt % of PBPT (50 mol % TP unit), the peak position of the  $\alpha$ -relaxation shifted toward lower temperatures with decreasing PBPT MW and new relaxation peaks were observed at ca.10°C. The new relaxation peak be-

came larger with increasing PBPT MW, but the positions of the new  $\alpha'$ -relaxation hardly changed (Fig. 8). In the modification with lower MW (7300) PBPT containing 50 mol % TP unit, the  $\alpha'$ -relaxation peak became shoulder, which indicates that the lower MW PBPT have higher miscibility with the epoxy matrix than the higher MW materials. The storage moduli at room temperature were comparable with or larger than for the unmodified resin.

### DISCUSSION

PBP and the related copolyesters are effective modifiers for improving the toughness of the highly cross-linked epoxy resins. All polyesters used in this study are soluble in the epoxy resin without solvents. PBP was most effective among them. The optimum composition for the modification was inclusion of 20 wt % of polyesters in every case (Fig. 1). Furthermore, the effectiveness of modifiers depends largely on polyester MW (Figs. 2 and 3). The in-



**Figure 6** FE-SEMs of the cured resins. (A) Control; (B) 20 wt % addition of PBP (MW 16,500).

teresting and characteristic results in the modification of epoxies with various kinds of the polyesters were as follows.

The use of 20 wt % PBP (MW 16,300) led to a 120% increase in  $K_{IC}$  at no expense of its mechanical and thermal properties, and the modified resin had the nanometer-order particulate structure [Fig. 6(B)]. The fracture enhancement behavior in the higher MW PBP-modified resins was similar to that in lower MW PBP-modified materials, but flexural properties for the former resins deteriorated compared with those for the latter (Table II, B19 and B02). PBPT having 50 mol % TP unit became white solid materials, and fracture enhancement behavior in the PBPT (50 mol % TP unit)-modified resin was similar to those in the other PBPT-modified materials, but flexural properties decreased (Table II, BT10, 11, and 06). PBP (50 mol % ND unit) were white solid ma-

terials, and its efficiency as modifiers was similar to PBPT (50 mol % TP unit), but flexural properties of the PBP (50 mol % ND unit)-modified resins maintained that of the unmodified resin (Table II, EN14).

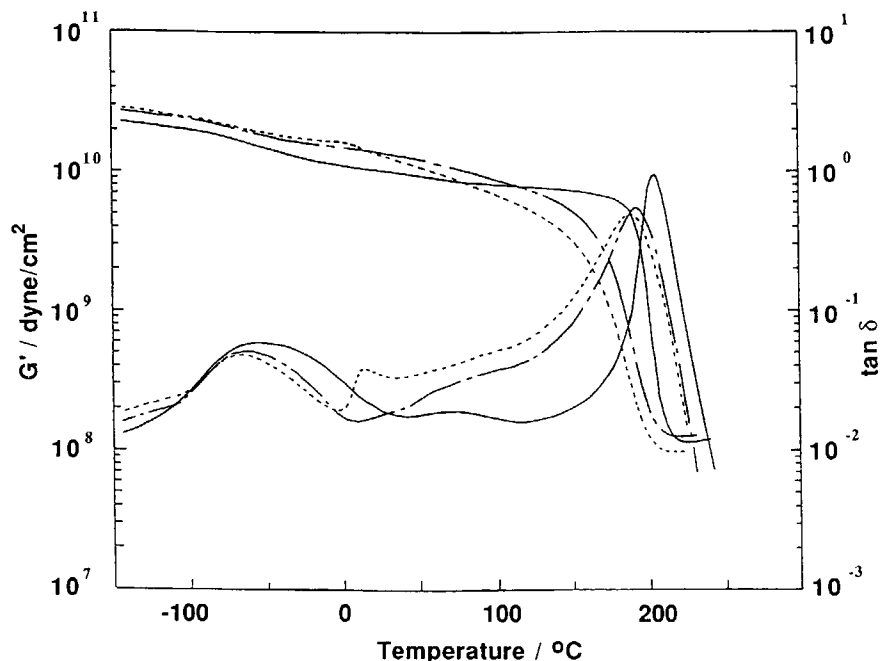
The toughening mechanism can be explained in terms of the morphological and dynamic viscoelastic behaviors.

It is well known that the toughening of epoxy resins is based on the microphase-separation structure of the cured resin in the modification of epoxy resins with reactive liquid rubbers<sup>1</sup> or reactive acrylic elastomers.<sup>4-8</sup> The elastomer particles having a diameter of a few microns were dispersed in the epoxy matrix in the more effective modification systems. The toughening in the modification with elastomers could be attained by dissipating the fracture energy mainly because of two process: 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 bluntness, and 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.<sup>3,15</sup> We also reported that various kinds of thermoplastics were effective modifiers and that the toughening of epoxies could be attained based on the cocontinuous phase structure.<sup>18,20-24</sup>

PEP and the related copolyesters were effective modifiers for highly cross-linked epoxies as reported previously,<sup>26</sup> and the toughening mechanism was discussed in detail. It was thought that the toughening of epoxies in the modification with PEP and the related copolyesters would be achieved by the particulate structure and that three factors would act mainly to improve the brittleness of epoxies: the reinforcement of the matrix itself because of incorporation of the polyesters, the high extent of dispersion of fine polyester-rich particles (<1  $\mu\text{m}$  diameter), and the existence of the new relaxations at ca.40 and 90°C. The toughening mechanism in the modification of epoxies with PBP and the related copolyesters is thought to be similar to that in the PEP modification systems as follows.

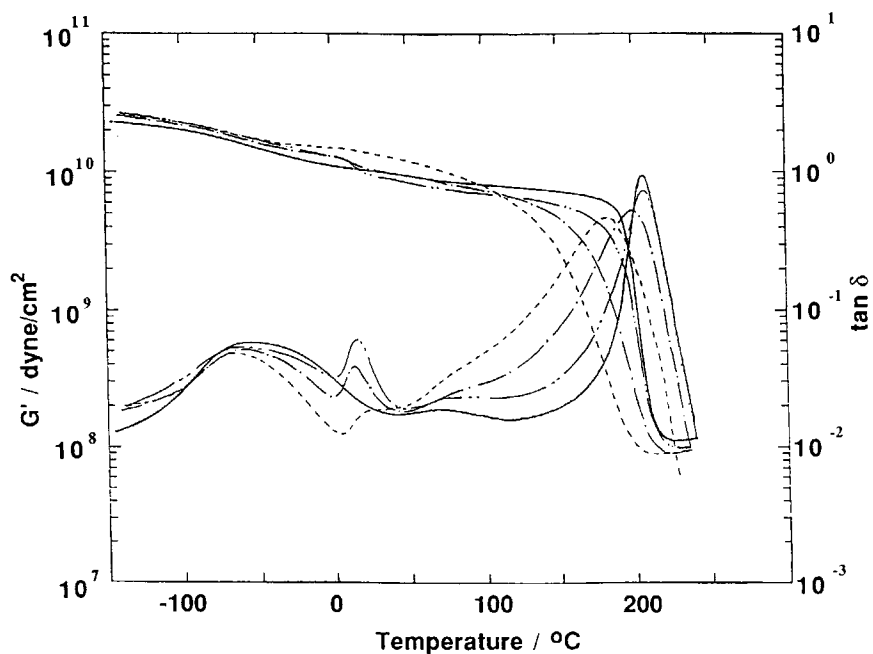
Poly(ethylene terephthalate) (PET) is an interesting material as a modifier for epoxies in terms of its mechanical properties but has poor



**Figure 7** Dynamic viscoelastic analysis for unmodified and PBP-modified resins. (—) control; (---) PBP (MW 16,300) 10 wt % addition; (-.-) PBP (MW 16,300) 20 wt % addition.

miscibility with epoxies. PEP has a similar structure to PET and is soluble in the epoxies without solvents. Recently, poly(butylene terephthalate)

(PBT) was used as an effective modifier for epoxies.<sup>27</sup> PBP has a similar structure to PBT but has higher miscibility to epoxies than PBT. The



**Figure 8** Dynamic viscoelastic analysis for unmodified and PBPT-modified resins. PBPT (50 mol % TP unit) 20 wt % addition, (—) control; (---) PBPT (MW 7300); (-.-) PBPT (MW 9900); (· · ·) PBPT (MW 15,600).

effectiveness of PBP as a toughener was comparable with that of PEP. In the modification with PBP and the related copolyesters, some of the modified resins had similar structures to those in the PEP modification, but conventional SEM was unsuitable to identify the microstructure of the modified resin in some cases. The difference in morphology between the PEP- and PBP-modified resins can be explained in terms of the solubility parameter (SP): the SP values ( $\text{MJ}/\text{m}^3$ )<sup>1/2</sup> for the epoxy resin, PEP, and PBP are 21.68, 25.40, and 23.96, respectively (by Fedors' method<sup>28</sup>). The SP value indicates that PBP has higher miscibility with the epoxy than PEP. Furthermore, dynamic viscoelastic analysis indicates that PBP and the related copolyesters would be dissolved into the epoxy matrix more than PEP. It is thought that the larger amount of the incorporated polyesters would lead to a greater improvement in the brittleness of the matrix itself because of the elastic properties of PBP. The modification results indicate that the reinforcement of the epoxy matrix itself by the incorporated polyesters would make a relatively large contribution to the toughening in the PBP modification than the PEP modification.

Furthermore, the existence of the  $\alpha'$ -relaxation near room temperature is one of the most important factors to reduce the brittleness of epoxies in the PBP modification system. When using PBP and the related copolyesters, the  $\alpha'$ -relaxation peaks based on the modifiers were observed in the region of  $T_g$  of the aromatic polyesters by dynamic viscoelastic analysis. 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.<sup>29,30</sup> We also reported that several relaxations at more than 50°C contribute to toughening of epoxies in the modification of the DDS-cured DGEBA resins with butyl acrylate-glycidyl acrylate copolymers.<sup>6</sup>

The toughening of epoxies in the present modification would then be achieved because of the above three factors. Among them, the contribution of the reinforcement of the matrix would be more important, considering miscibility of PBP and fracture-enhancement behavior in the lower MW PBP modification systems. Such modification behaviors are similar to those in the DGEBA/acid anhydride/aromatic polyester systems.<sup>25</sup> It is noteworthy that the optimum mor-

phology, the cocontinuous or inverted phase structure, in the modification of epoxies with thermoplastics could not be obtained in more complicated geometrics such as those found in a composite and that the nanometer-order particulate structure would be more favorable in such a constrained matrix.

$T_g$ s for the modified resins were equal or slightly lower than the parent resin.

## CONCLUSIONS

PBP and the related copolyesters are effective modifiers for improving the toughness of epoxy resins. Their effectiveness depended on polyester structure, MW, and content. The toughening mechanism in the present modification is due to two-phase separation structures as well as in the PEP modification. Their efficiency as modifiers is due to three causes: the reinforcement of the matrix itself by the incorporated polyesters, the existence of the new relaxations at ca.10°C and the broadness of the  $\alpha$ -relaxation peak, and the high extent of dispersion of fine polyester-rich particles. The more suitable compositions for the modification of the epoxy resin were inclusion of 20 wt % PBP (MW 16,300), where  $K_{IC}$  increased 120% with no loss of mechanical and thermal properties.

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