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TOUGHENING OF AROMATIC DIAMINE-CURED EPOXY RESINS BY POLY(ETHYLENE PHTHALATE)S AND THE RELATED COPOLYESTERS

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Abstract—Aromatic polyesters, prepared by the reaction of aromatic dicarboxylic acids and 1,2-ethanediol, were used to improve the toughness of bisphenol-A diglycidyl ether epoxy resin cured with *p,p′*-diaminodiphenyl sulphone. These polyesters contained poly(ethylene phthalate)s, poly(ethylene phthalate-co-ethylene isophthalate)s (PEPI), poly(ethylene phthalate-co-ethylene terephthalate)s, and poly (ethylene phthalate-co-ethylene 2,6-naphthalene dicarboxylate)s. All the 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 epoxy resin. For example, the inclusion of 20 wt% of PEPI (10 mol.% isophthalate unit, MW 7400) led to a 100% increase in the fracture toughness (K_{IC}) of the cured resin with no loss of mechanical and thermal properties. The modified resins had a two-phase morphology and the polyester-rich dispersed particles in the epoxy matrix. The toughening mechanism was discussed in terms of the morphological and dynamic viscoelastic behaviours of the modified epoxy resin system.

INTRODUCTION

Epoxy resins are one of the most important thermosetting polymers and have wide use as structural adhesives and matrix resin for fibre 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 (CTBN) [1] or terminally functionalized engineering thermoplastics [2, 3]. In previous papers, various kinds of epoxide-containing acrylic elastomers have been reported as improving the toughness of *p,p′*-diaminodiphenyl sulphone (DDS)-cured epoxy resins, where vinylbenzyl glycidyl ether and glycidyl (meth)-acrylate were used as epoxy containing monomers [4–8].

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. At first commercial poly(ether sulphone)s (PES), such as Victrex, were used as modifiers in the modification of polyfunctional epoxies, such as tetraglycidyl-4,4′-diaminodiphenyl methan (TGDDM), but were found to be less effective owing both to the highly cross-linked structure and to the poor interfacial bonding between the two uncompatibilized phases in the cured resin [9–11]. Terminally functionalized polysulphones are more effective modifiers than commercial grades of PES used as thermoplastic materials [2, 12]. Most recently, polysulphones containing pendant amino groups have been reported as effective modifiers [13]. Other engineering thermoplastics have also been examined as modifiers, where poly(etherimide)s [3, 14–16], poly(aryl ether ketones)s [17, 18], poly(phenylene oxide) [19] have been reported as effective modifiers. We have found that *N*-phenylmaleimide-styrene copolymers (PMS) and *N*-phenylmaleimide - *N* - cyclohexylmaleimide - styrene terpolymers were effective modifiers for diglycidyl ether of bisphenol-A (DGEBA) [20, 21]. PMS was also an effective modifier for the liquid aminocresol type trifunctional epoxy resin [22].

In a previous paper [23] we have reported that aromatic polyesters, prepared by the reaction of (iso)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, hence it is interesting to investigate how aromatic polyesters would behave in highly cross-linked matrices. This paper reports the modification of DDS-cured DGEBA resins with aromatic polyesters such as poly(ethylene phthalate)s (PEP) and the related copolyesters. These polyesters are soluble in the epoxy resin without using solvents. The effect 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 bisphenol-A diglycidyl ether (DGEBA) (Epikote 828, Shell Chemical Industrial

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Co., epoxy equivalent weight 190). DDS was used as a curing agent. The aromatic polyesters were prepared by the reaction of 1,2-ethanediol and aromatic dicarboxylic acids as reported previously [23]. Aromatic dicarboxylic acid and the derivatives contained phthalic anhydride, isophthalic acid, dimethyl terephthalate and dimethyl 2,6-naphthalene dicarboxylate. Dimethyl 2,6-naphthalene dicarboxylate was provided by Mitsubishi Gas Chemical Corp. Other reagents were used as received.

Measurements

^{1}H-NMR spectra were recorded on a 90 MHz instrument (JEOL JNM-9MX 90) using $CDCl_3$ 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 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_g's) of both polyesters and cured resins were measured as the onset temperatures by differential scanning calorimetry (Shimadzu DSC 41M type) at a heating speed of 10°C/min. Scanning electron micrographs (SEM) were taken with a Hitachi SEM S-2100A instrument using failed specimens in the K_{IC} tests. Dynamic viscoelastic analysis was performed with a Rheometrics RDS-II type (Rheometrics Co.) between −150 and 250°C at a heating speed of 5°C/min at frequency of 1 Hz.

Curing procedure

The aromatic polyester was dissolved into the epoxy resin without solvents by heating at 140°C. Then the curing agent, DDS, was added to the mixture, which was kept at 130°C for about 1 hr to dissolve DDS. The resulting clean mixture was poured into a silicone rubber mould preheated at 120°C. The curing cycle was 1 hr at 120°C and 5 hr at 180°C. The amount of DDS used was stoichiometrically calculated to fully react with 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 1,2-ethanediol and aromatic dicarboxylic acid or the derivatives and used as modifiers, which contain poly(ethylene phthalate)s (PEP), poly(ethylene phthalate-co-ethylene isophthalate)s (PEPI), poly(ethylene phthalate-co-ethylene terephthalate)s (PEPT), and poly(ethylene phthalate-co-ethylene 2,6-naphthalene dicarboxylate)s (PEPN). The polyester compositions were equal to the feed compositions by ^{1}H-NMR spectroscopy. Table 1 reports some characteristic properties of the aromatic polyesters. The GPC-average molecular weight (M_{GPC}) was used as a measure of the molecular weight (MW) in this paper as well as in the previous paper [23], 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.

Mechanical and thermal properties of modified epoxy resins

Table 2 shows the representative results for the modification of the epoxy resin with the aromatic polyesters. The cured parent epoxy resin was transparent, but the modified resins became opaque during curing.

Figures 1 and 2 show the mechanical and thermal properties of the modified resins as a function of concentration of polyesters. The K_{IC} values for the modified resins increased linearly up to 20 wt% addition of polyesters (Fig. 1). The fracture enhancement behaviour in the polyesters-modified resins was similar except for PEPN, which was less effective and the K_{IC} values were lower. In general, the flexural strength for the modified resins was maintained and the flexural moduli were comparable or lower than that for the parent epoxy resin. It is noteworthy

Table 1. Preparation and characterization of aromatic polyesters

Entry No.	Polyester[a] composition	Yield (%)	M_{GPC}[b] (10^3)	M_n[b] (10^3)	M_w[b] (10^3)	M_w/M_n	T_g[c] (°C)	Acid content[d] (m-equiv/g)
PEP 13	—	94	6.8	5.8	8.0	1.40	—	—
5	—	95	8.1	6.0	9.6	1.62	8	0.011
10	—	94	10.3	7.3	12.2	1.67	32	0.008
11	—	96	21.0	16.0	25.0	1.61	—	—
PEPI 1	IP 10	96	7.4	5.4	8.8	1.62	31	0.021
5	10	95	12.0	9.2	14.0	1.54	30	0.011
4	10	91	25.0	19.0	30.0	1.62	41	—
6	20	97	6.3	5.1	7.5	1.46	31	0.005
8	20	96	11.0	8.3	13.0	1.54	40	—
2	20	95	17.2	12.0	20.0	1.73	—	—
PEPT 1	TP 10	98	5.2	4.0	6.3	1.60	28	—
3	10	95	10.6	7.5	13.0	1.74	39	—
2	10	—	14.2	9.8	16.5	1.68	—	—
4	20	98	6.8	5.3	8.4	1.60	42	—
PEPN 1	ND 10	98	8.3	6.0	10.0	1.66	38	—
4	10	—	15.5	10.4	18.7	1.80	—	—
3	20	94	16.5	10.0	19.6	1.89	—	—

[a] mol.%. IP: isophthlate unit, TP: terephthalate unit, ND: 2,6-naphthalene dicarboxylate unit.
[b] By GPC.
[c] By DSC.
[d] Terminal carboxyl contents of polyesters.

Table 2. Physical properties of modified epoxy resins

Entry No.	Polyester[a] No.[b]	Polyester[a] Composition (mol.%)	Polyester[a] MW (10^3)	K_{IC}[c] (MN/m$^{3/2}$)	n[d]	Flexural properties Strength[c] (kgf/mm^2)	Flexural properties (MPa)	Flexural properties Modulus[c] (kgf/mm^2)	Flexural properties (GPa)	Flexural properties n[d]	T_g[e] (°C)
Control			—	0.70 ± 0.05	5	13.8 ± 0.4	135	351 ± 15	3.44	5	180
PEP series											
19	PEP13	—	6.8	1.19 ± 0.07	6	15.8 ± 0.4	155	333 ± 17	3.27	6	—
2	PEP5	—	8.1	1.57 ± 0.04	6	13.2 ± 0.3	129	253 ± 7	2.48	6	165
6	PEP10	—	10.3	1.44 ± 0.04	5	14.8 ± 0.3	145	339 ± 12	3.32	6	180
18	PEP11	—	21.0	1.15 ± 0.06	6	14.7 ± 0.3	144	331 ± 16	3.25	6	—
PEPI series											
10	PEPI1	IP 10	7.4	1.43 ± 0.02	4	18.3 ± 0.3	179	436 ± 9	4.28	7	170
21	PEPI5	10	12.0	1.54 ± 0.08	6	15.5 ± 0.5	152	347 ± 18	3.40	5	170
17	PEPI4	10	25.0	1.15 ± 0.06	5	14.7 ± 0.7	144	348 ± 5	3.41	5	177
22	PEPI6	20	6.3	1.47 ± 0.06	5	17.1 ± 0.5	168	376 ± 9	3.69	6	134
23	PEPI8	20	11.0	1.27 ± 0.08	5	14.3 ± 0.4	140	356 ± 19	3.49	6	157
12	PEPI2	20	17.2	1.15 ± 0.06	6	16.9 ∓ 0.3	166	363 ± 5	3.56	5	176
PEPT series											
25	PEPT1	TP 10	5.2	1.25 ± 0.01	4	14.9 ± 0.3	146	330 ± 9	3.24	5	149
26	PEPT3	10	10.6	1.41 ± 0.07	4	14.4 ± 0.2	141	329 ± 9	3.23	6	170
33	PEPT2	10	14.2	1.21 ± 0.08	4	14.6 ± 0.2	143	342 ± 8	3.35	6	178
27	PEPT4	20	6.8	1.25 ± 0.04	4	—	—	—	—	—	166
PEPN series											
28	PEPN1	MD 10	8.3	1.21 ± 0.06	4	15.6 ± 0.4	153	372 ± 17	3.65	6	166
32	PEPN4	10	15.5	1.18 ± 0.06	5	15.9 ± 0.6	156	347 ± 6	3.40	6	172
31	PEPN3	20	16.5	1.13 ± 0.06	4	15.7 ± 0.7	154	349 ± 6	3.42	5	—

[a] Polyester content 20 wt%.

[b] Entry number in Table 1.

[c] The ± x values show standard deviation.

[d] Number of specimens tested.

[e] By DSC.

that the flexural strength and modulus for the PEPI (10 mol.% isophthalate (IP) unit, MW 7400)-modified resins were larger than those for the parent resin. The T_g values for the modified resins were equal or slightly lower than that for the parent resin.

Figures 3 and 4 show the dependence of the mechanical and thermal properties for the modified resins of 20 wt% addition on polyester MW. In the modification with the polyesters, K_{IC} increased with increasing MW and then decreased except for the modification with PEPN. The optimum MW of the polyesters depended on the polyester structure. K_{IC} for the PEP (MW 8100)-modified resin increased 120% at no deterioration of flexural strength and only slight reduction in T_g (Entry No. 2 in Table 2). The use of PEPI (MW 7400) with 10 mol.% IP unit led to a 120% increase in K_{IC} at no expense of flexural strength, modulus and T_g (No. 10). At 20 wt% addition of PEPI (20 mol.% IP unit, MW 6300), the K_{IC}

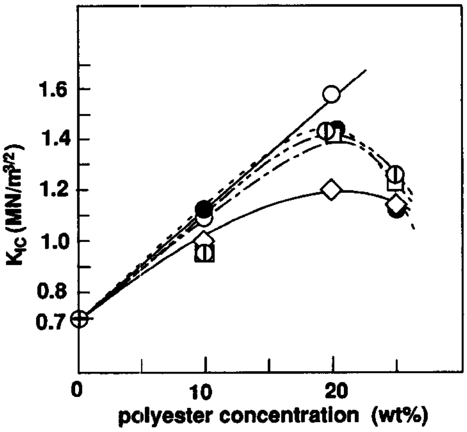

Fig. 1. Fracture toughness for the modified resins as function of polyester concentration. ⊕ Control; ○ PEP(MW 8100); ● PEP(MW 10,300); □ PEPI(10 mol.% IP unit, MW 7,400); ⦶ PEPT(10 mol.% TP unit, MW 10,600); ◇ PEPN(10 mol.% ND unit, MW 8300).

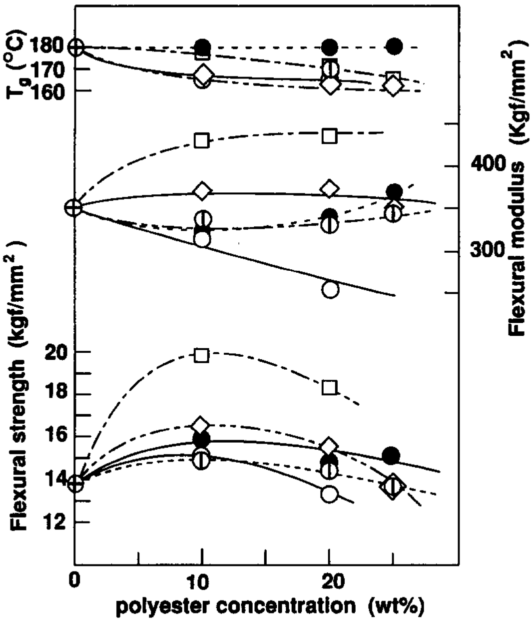

Fig. 2. Physical properties of the modified resins as function of polyester concentration. ⊕ Control; ○ PEP(MW 8100); ● PEP(MW 10,300); □ PEPI(10 mol.% IP unit, MW 7400); ⦶ PEPT(10 mol.% TP unit, MW 10,600); ◇ PEPN(10 mol.% ND unit, MW 8300).

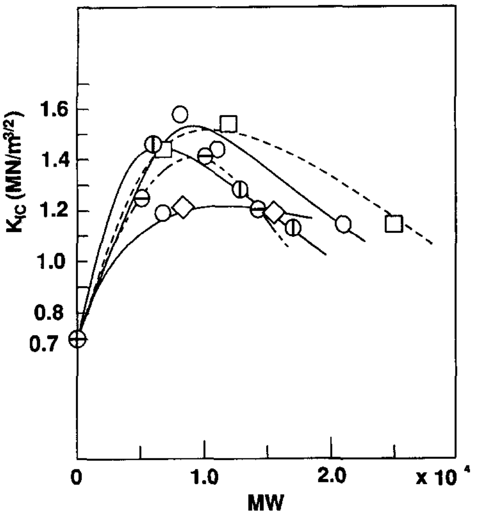

Fig. 3. Dependence of fracture toughness for the modified resins on polyester molecular weight. 20 wt% modifier addition. ⊕ Control; ○ PEP: □ PEPI(10 mol.% IP unit); ⦶ PEPI(20 mol.% IP unit); ⊖ PEPT(10 mol.% TP unit); ◇ PEPN(10 mol.% ND unit).

value increased 100% at no loss of flexural properties but T_g decreased (No. 22). When using 20 wt% of PEPT (10 mol.% terephthalate (TP) unit, MW 10,600), K_{IC} increased 100% with no reduction of flexural properties and T_g (No. 26). The use of PEPT (20 mol.% TP unit, MW 6800) resulted in a 80% increase in K_{IC} and a 14°C decrease in T_g (No. 27). PEPN (10 mol.% 2,6-naphthalene dicarboxylate (ND) unit) were less effective since the inclusion of 20 wt% of PEPN (10 mol.% ND unit, MW 8300) gave only a 70% increase in K_{IC} (No. 25).

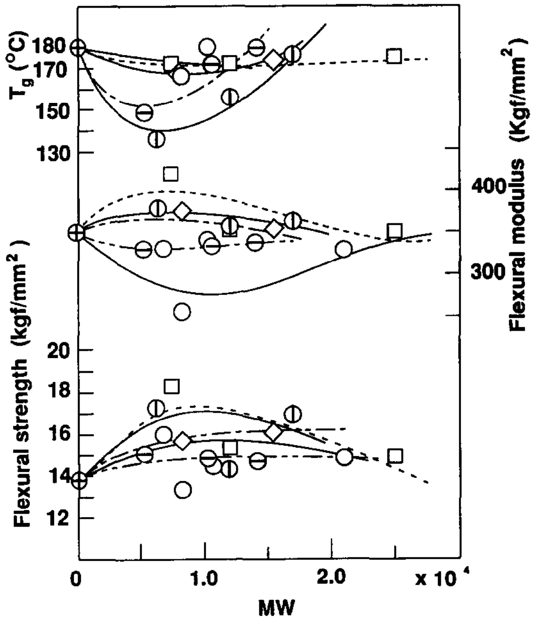

Fig. 4. Dependence of physical properties for the modified resins on polyester molecular weight. 20 wt% modifier addition. ⊕ Control; ○ PEP □ PEPI(10 mol.% IP unit); ⦶ PEPI(20 mol.% IP unit): ⊖ PEPT(10 mol.% TP unit); ◇ PEPN(10 mol.% ND unit).

Morphologies of the modified epoxy resins

The morphologies of the cured resins were investigated by scanning electron microscopy (SEM)s. Figures 5–8 show SEM micrographs for the modified resins. The morphological results are collected in Table 3. The parent epoxy resins had only one phase as reported previously [4]. The inclusion of polyesters led to two phase morphologies with polyester-rich spherical particles dispersed in the epoxy-rich matrix. In the modification with PEP the average diameter (D) of dispersed particles increased with increasing PEP content (Table 3, Entry Nos 5, 6 and 11, and

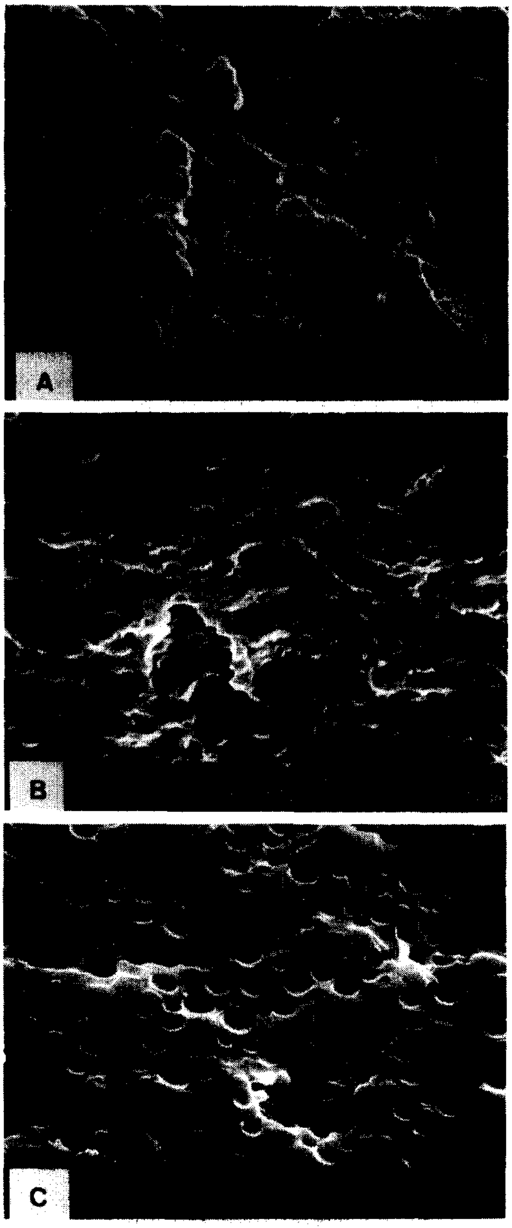

Fig. 5. SEMs of fracture surfaces for PEP-modified resins. Amount of PEP (MW 10,300): (A) 10 wt% addition: (B) 20 wt% addition; (C) 25 wt% addition.

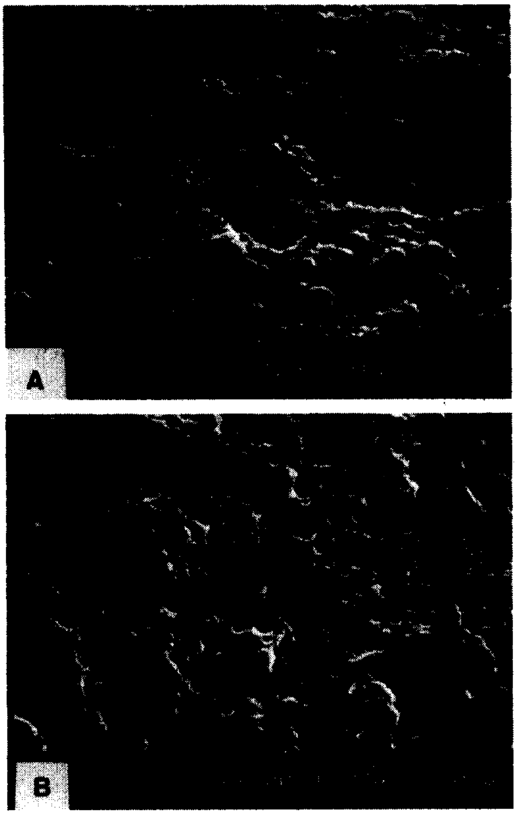

Fig. 6. SEMs of fracture surfaces for PEPI-modified resins. Amount of PEPI (10 mol.% IP unit, MW 7400): (A) 20 wt% addition: (B) 25 wt% addition.

Fig. 5) and the volume fraction (V_f) of precipitated particles tended to increase with an increase in PEP MW (Nos 19, 2 and 6). The volume fraction for the higher MW (21,000) PEP-modified resins decreased slightly (No. 18), compared with that for the medium MW (10,300) PEP-modified materials.

The particle size and the volume fraction for PEPI (10 mol.% IP unit)-modified resins increased with increase in PEPI MW (Nos 10, 21 and 17, and Fig. 6) and content (Nos 9, 10 and 15). The use of PEPI (20 mol.% IP unit, MW 6300) led to a morphology having ill-defined fine dispersed particles (No. 22 and Fig. 7A). The average particle diameters and the volume fraction for modification with higher MW (12,000 or 17,000) PEPI (20 wt%) of 20 mol.% IP unit were smaller than those for PEP-modified resins (Nos 23 and 6, Figs 7B and 6B).

The morphology of PEPT- and PEPN-modified resins are shown in Fig. 8. The average diameter and the volume fraction of the particles increased with increasing PEPT (10 mol.% TP unit) MW (Nos 25, 26 and 33) and content (Nos 25, 29 and 26). The particle sizes for PEPN (10 mol.% ND unit)-modified resins tended to increase with increasing PEPN MW (Nos 28 and 32).

In general, the polyesters used in this study have high miscibility with the epoxy matrix and their miscibility decreased with increase in MW, except for PEP (MW 21,000). The miscibility of PEPI (20 mol.% IP unit) is higher than the other polyesters. It is noteworthy that except for PEPI (20 mol.% IP unit, MW 6300) particles less than 1 μm in diameter dispersed homogeneously in every case and that the particle size distribution was small.

Dynamic viscoelastic analysis of modified epoxy resins

Figures 9–12 show the storage modulus, G', and tan δ curves for the unmodified and modified resins. In the modification with PEP of MW 8100, the peak position of the α-relaxation in the tan δ curve is shifted towards lower temperature, and new relaxations appear at *ca* 40 and 90°C. The α-relaxation shifts towards lower temperature and the magnitude of the new relaxation peak at 40°C (α'-relaxation) increases with increasing PEP content (Fig. 9). When using 20 wt% of higher MW PEP (10,300), the peak position of the α-relaxation for the modified resin shifts towards slightly lower temperatures, compared to that for the unmodified resin. The peak position of the α'-relaxation shifted slightly towards higher temperature with increasing PEP MW. The storage moduli at room temperature were equal to that for the unmodified resin.

In the modification with 20 wt% of PEPI (10 mol.% IP unit), the peak position of the α-relaxation shifts slightly towards lower temperatures and two new relaxation peaks are also observed, but the positions and magnitude of both the α-relaxation and the new α'-relaxation are independent of the MW of PEPI (Fig. 10). In the modification with lower MW (6300) PEPI containing 20 mol.% IP unit, the peak

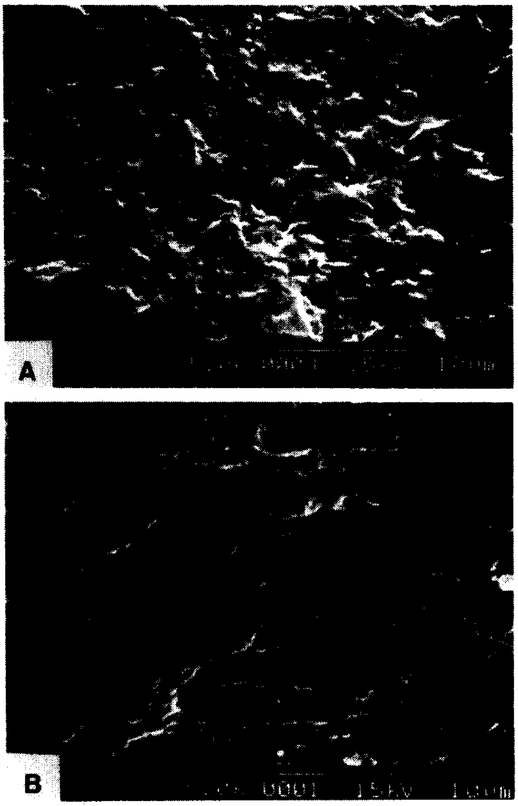

Fig. 7. SEMs of fracture surfaces for PEPI-modified resins. (A) PEPI (20 mol.% IP unit, MW 6300), 20 wt% addition; (B) PEPI (20 mol.% IP unit, MW 12,000), 20 wt% addition.

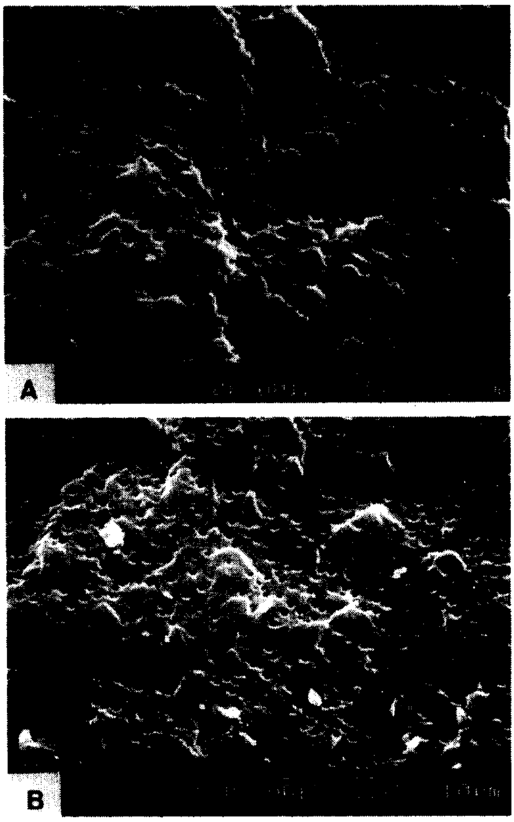

Fig. 8. SEMs of fracture surfaces for PEPT-or PEPN-modified resins. (A) PEPT (10 mol.% TP unit, MW 10,600), 20 wt% addition; (B) PEPN (10 mol.% ND unit, MW 8300), 20 wt% addition.

position of the α-relaxation shifts towards lower temperature and the peak is broader, compared to the peak for the higher MW (17,000) PEPI-modified resin (Fig. 11), which indicates that the former PEPI have higher miscibility with the epoxy matrix than the latter, as shown in the morphological results. The storage moduli at room temperature were comparable to that for the unmodified resin.

Figure 12 shows the dynamic viscoelastic results in the modification with 20 wt% of PEPT (10 mol.% TP unit). The peak position of the α-relaxation in the tan δ for the PEPT-modified resins shifts towards higher temperature with increasing PEPT MW. New α′-relaxation peaks were also observed in the similar temperature region to the previous polyesters. The peak positions of the α′-relaxation are independent of the MW of PEPT. The magnitude of peak of the relaxation at *ca* 90° decreased with increasing PEPT MW because of a decrease in miscibility of higher MW PEPT. The storage moduli at room temperature were equal to or larger than that for the unmodified resin. The peak position and magnitude of the α-relaxation in the tan δ for the PEPN (10 mol.% ND unit, MW 8300)-modified resins were similar to those for the PEPT (10 mol.% TP unit, MW 10,600)-modified resins, but the α′-relaxation peak position of the former shifted towards somewhat higher temperature than that of the latter.

DISCUSSION

Aromatic polyesters are found to be effective modifiers for improving the toughness of the highly cross-linked epoxy resins. PEP, PEPI and PEPT have

Table 3. Morphological results

Entry No.	Polyester: Composition	Polyester: MW	Resin composition: Matrix/polyester	D[a] (μm)	V_f^b	N[c] (10^2)
	—	—	100/0	—	—	—
PEP series						
19	—	6800	80/20	0.27 ± 0.08	0.155	2.5
2	—	8100	80/20	0.37 ± 0.11	0.226	1.9
5	—	10,300	90/10	0.23 ± 0.07	0.117	2.5
6	—	10,300	80/20	0.52 ± 0.17	0.238	1.4
11	—	10,300	75/25	0.92 ± 0.30	0.394	0.6
18	—	21,000	80/20	0.51 ± 0.19	0.180	0.8
PEPI series						
9	IP 10	7400	90/10	0.28 ± 0.10	0.149	2.2
10	10	7400	80/20	0.29 ± 0.09	0.237	3.6
15	10	7400	75/25	0.40 ± 0.12	0.314	2.3
21	10	12,000	80/20	0.33 ± 0.11	0.250	2.7
17	10	25,000	80/20	0.58 ± 0.17	0.280	1.0
22	20	6300	80/20	—[d]	—[d]	—[d]
23	20	12,000	80/20	0.31 ± 0.11	0.186	1.3
12	20	17,000	80/20	0.39 ± 0.14	0.182	1.1
PEPT series						
25	TP 10	5200	80/20	0.13 ± 0.05	0.079	4.1
29	10	10,600	90/10	0.18 ± 0.05	0.085	3.0
26	10	10,600	80/20	0.37 ± 0.11	0.256	2.3
30	10	10,600	75/25	0.61 ± 0.16	0.324	1.0
33	10	14,200	80/20	0.46 ± 0.13	0.335	1.9
27	20	6800	80/20	0.17 ± 0.06	0.119	4.8
PEPN series						
28	ND 10	8300	80/20	0.30 ± 0.08	0.158	2.1
32	10	15,500	80/20	0.43 ± 0.11	0.308	2.0
31	20	16,500	80/20	0.46 ± 0.15	0.339	1.9

[a] Average particle diameter.
[b] Volume fraction of dispersed particles.
[c] Number of particles/100 μm^2.
[d] There are ill-defined dispersed particles.

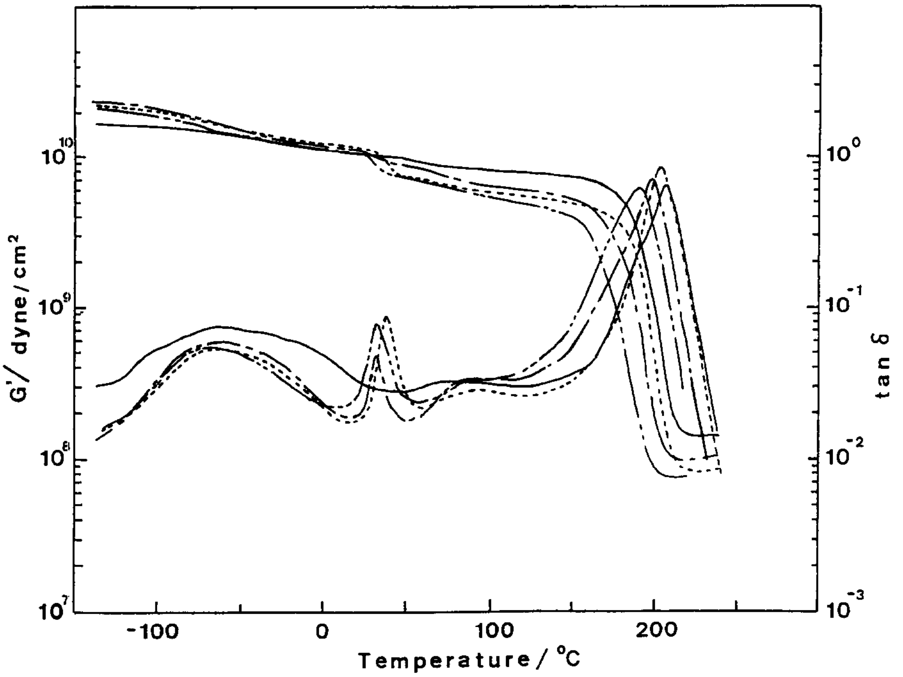

Fig. 9. Dynamic viscoelastic analysis for unmodified and PEP-modified resins. (——) Control; (— — —) PEP (MW 8100), 10 wt% addition; (— — — —) PEP (MW 8100), 20 wt% addition; (- - - - - -) PEP (MW 10,300), 20 wt% addition.

similar efficiency, but PEPT is slightly less effective. All the polyesters used in this study are soluble in the epoxy resin without solvents. The T_g's of the polyesters increases slightly by introducing rigid structures in the backbone, but their effectiveness as modifiers were rather insensitive to the polyester structure and depended on the polyester MW and concentration. The optimum composition for the modification was inclusion of 20 wt% of polyesters in every case (Figs 1 and 2). Furthermore the effectiveness of modifiers depends largely on polyester MW (Figs 3 and 4). The interesting and characteristic

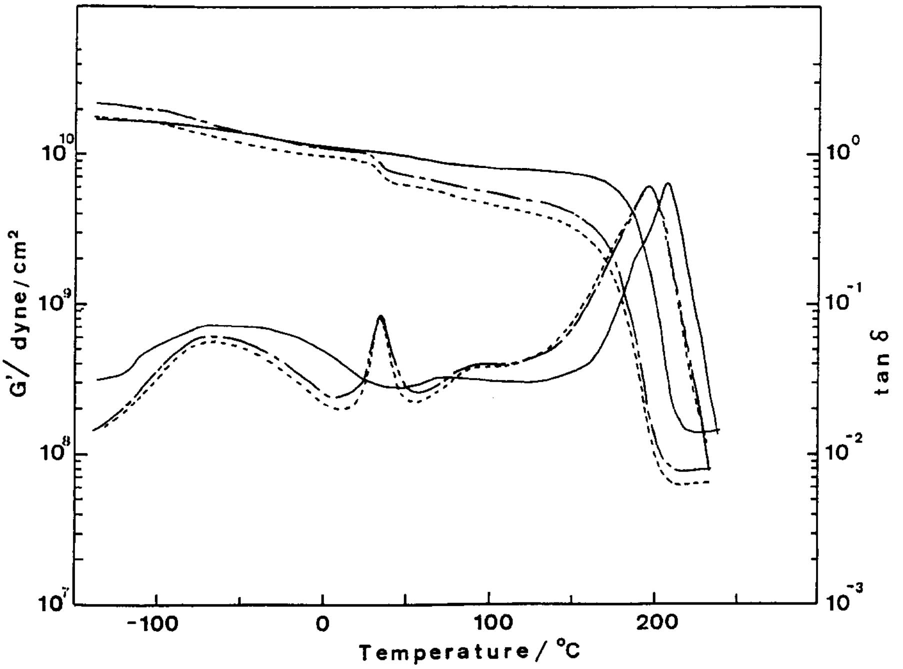

Fig. 10. Dynamic viscoelastic analysis for unmodified and PEPI-modified resins. PEPI (10 mol.% IP unit) 20 wt% addition. MW of PEPI: (——) Control; (- - - -), MW 7400 (— — —), MW 12,000.

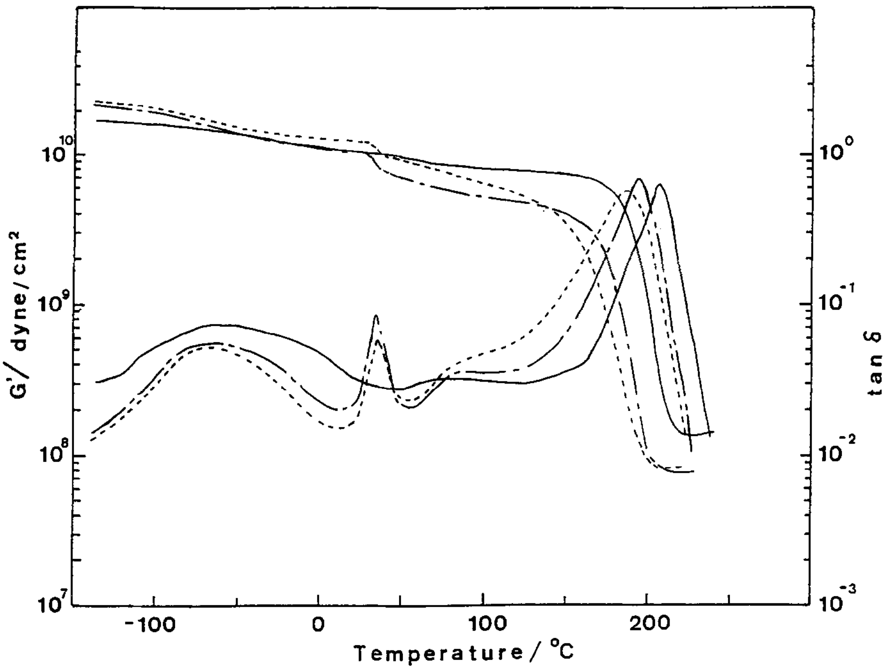

Fig. 11. Dynamic viscoelastic analysis for unmodified and PEPI-modified resins. PEPI (20 mol.% IP unit) 20 wt% addition. MW of PEPI: (——), control; (- - - -) MW 6300; (— — —) MW 17,000.

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

The use of 20 wt% of PEP (MW 10,300) led to a 120% increase in K_{IC} at no expense of its mechanical and thermal properties. When using 20 wt% of PEPI (10 mol.% IP unit, MW 7400), K_{IC} for the modified resin increased 100% with no sacrifice of thermal properties, where flexural strength and modulus at room temperature increased compared to those for the parent epoxy resin. In the modification with high MW (12,00) PEPI (10 mol.% IP unit), K_{IC} increased 120% at no loss of flexural and thermal properties. The inclusion of low MW (6300) PEPI (20 mol.% IP unit) resulted in 110% increase in K_{IC} with no

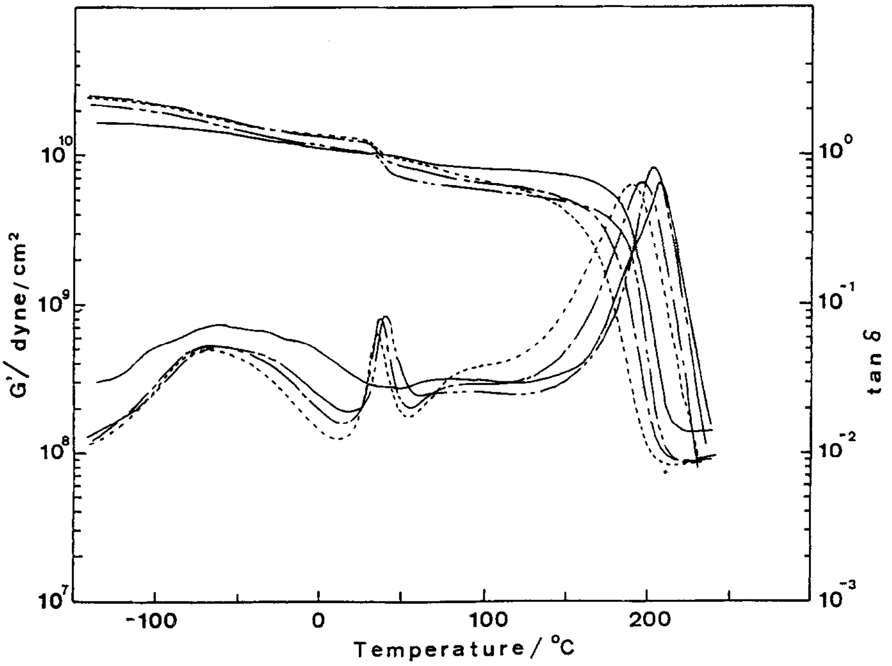

Fig. 12. Dynamic viscoelastic analysis for unmodified and PEPT-modified resins. PEPT (10 mol.% TP unit) 20 wt% addition. MW of PEPT: (——) control; (- - - -) MW 5200; (— — —) MW 10,600; (— — — —) MW 14,200.

reduction in flexural properties, but the T_g for the modified resin decreased considerably. These results are in agreement with the morphological and dynamic viscoelastic behaviours. This modified resin had different morphology from the others; there are ill-defined dispersed particles in the epoxy matrix (Fig. 7A) and the α-relaxation in the tan δ curve shifted towards lower temperature and became broader than that in the higher MW (17,000) PEP modification (Fig. 11). These results indicate that PEPI (20 mol.% IP unit, MW 6300) has high solubility with the epoxy matrix. In the modification with higher MW PEPI of 20 mol.% IP unit, the tendency to phase-separate is more significant and well-defined spherical particles were observed (Fig. 7B). PEPT (10 mol.% TP unit, MW 10,600) is a comparable effective modifier to PEP (MW 10,300), while PEPN (10 mol.% ND unit, MW15,500) is less effective.

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

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 [1] or reactive acrylic elastomers [4–8]. 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 because of the following various process. When the hydrostatic force is applied to specimens with an initial crack, particles in front of the crack tip act as stress concentrators; they cavitate and interact with each other. Such interaction between particles induces shear band near the crack and the crack tip is blunted by plastic shear deformation of the matrix. When the hydrostatic force increases, the crack propagate unstably, particles are elongated and torn, and crack deflection and bifurcation are brought about.

In the modification of epoxies with engineering thermoplastics, the most effective results can be obtained by the co-continuous 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, 14]. We have also reported that various kinds of thermoplastics were effective modifiers and that the toughening of epoxies could be attained based on the co-continuous phase structure [18, 20–22].

In the present modification system the fracture surfaces for the polyesters-modified resins were rough and ridgy. The modified resins have two-phase morphologies having well-defined spherical particles dispersed in the matrix except for the PEPI (20 mol.% IP unit, MW 6,300) and the particles sizes are rather fine (Table 3). The particle size distribution was also small and coagulation of the particles was hardly observed (Figs 5–8). It is thought that the toughening of epoxies in the present modification system can be attained by the two phase separation structure. Their efficiency as modifiers would be partly because of the high extent of disperion of fine particles less than 1 μm diameter.

In the modification of highly cross-linked epoxy matrices, reactive rubbers such as CTBN have been reported as ineffective modifiers, because the rubber-rich particles as stress concentrators induce the plastic shear deformation of the highly cross-linked matrix to a far less extent and the dissipation of the fracture energy by the enlargement of the deformation zone can be hardly attained [8, 24]. The reactive acrylic elastomers having pendant epoxy groups were more effective than CTBN and their use as modifiers has led to a greater increase in K_{IC} in the DGEBA/DDS system [4–7]. It is interesting that the modified resins in the present system have similar two-phase morphologies to the elastomer-modified resins, but the aromatic polyesters were more effective modifiers for the DDS-cured DGEBA resins with highly cross-lined structure (T_g, 180°C) (Table 2). The difference in effectiveness as the modifier between the reactive acrylic elastomers and the polyesters could be partly explained in terms of the existence of the α′-relaxation just above room temperature. The aromatic polyesters used in this study have T_g's somewhat higher than room temperature. The T_g's of the aromatic polyesters are intermediate between the reactive acrylic elastomers and the engineering thermoplastics. The thermal properties of the modifiers reflect the dynamic viscoelastic behaviours for the modified resins. The α′-relaxation peaks based on the modifiers were observed at *ca*, −20°C in the modification with butyl acrylate (BA)-glycidyl methacrylate (GMA) copolymers (T_g's, *ca*, −35°C) [6] or BA-GMA-acrylonitrile terpolymers (T_g's, *ca*, −35°C) [7]; the peak positions of the α′-relaxation shifted towards higher temperature because of the reaction of pendant epoxy groups and the matrix. In the present modification the well-defined α′-relaxation peak appeared in the region of T_g of the aromatic polyesters, which indicates that the polyesters dispersed in the matrix was restricted to a less extent by the chemical reaction of the polyesters and the epoxy matrix as described below. The new relaxation also appeared at *ca* 90°. This relaxation can be attributed to the formation of a matrix phase containing both the parent epoxy resin and dissolved PEP in various amounts. Ochi *et al.* shows that the presence of the relaxation peak near room temperature is effective in improving the toughness of the spiro-ring type epoxy resin because of the increase in the plastic deformation zone attributed to the increase in temperature at the crack front due to the presence of the β′-relaxation [25]. 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 BA-glycidyl acrylate copolymers [6]. Then the efficiency of the polyesters could be partly because of the existence of the relaxations.

In the previous paper [23] methyl hexahydrophthalic anhydride-cured epoxies with lightly cross linked structure were modified with aromatic polyesters such as PEP and poly(butylene phthalate)s (PBP). The fracture surfaces for the low MW PEP-modified resins were rough and ridgy, but no particle precipitated was observed by SEMs. There were irregular particles in the modification with PEP of MW more than 7200, but the volume fraction of the particles was much smaller than PEP content in the feed. The fracture surface was rough in the modification with PBP, but no particle existed. These results indicated that the aromatic polyesters were chemically reacted into the epoxy matrix itself in the curing with the acid anhydride. The low MW PEP and PBP modification systems are special cases, considering that the brittleness of the epoxy resin could be improved to a great extent in spite of not having microphase separation structure by SEMs. The modified resins may have the polyester-rich particles of the nanometer order, which could not be observed by SEMs. Poly(ethylene terephthalate) (PET) is an interesting material as a modifier for epoxies in terms of its mechanical properties, but have poor miscibility with epoxies. PEP has a similar structure to PET and are soluble in the epoxies without solvents. It is thought that the brittleness of the matrix itself could be improved by the incorporated polyesters because of the outstanding mechanical properties of PEP. Then we have reproted that the improved toughness of the PEP-modified resins would be partly due to the reinforcement of the epoxy matrix itself by the incorporated polyesters and partly due to the dissipation of the fracture energy by blunting the crack tip based on the delocalized plastic deformation near particles. The morphological results indicate that the most effective modification for the cured DGEBA resin could be achieved by the former mechanism in the acid anhydride curing system.

In the present modification system morphological and dynamic viscoelastic results indicate that the toughening based on the micro-phase separation would be more important for the improvement of the modified resins. The difference in the toughening mechanism between the two modification systems could be explained by the compatibility of the polyesters with the epoxy matrix. The dynamic viscoelastic analysis gave interesting information on such compatibility. In the acid anhydride curing system the α'-relaxation based on PEP has been observed at *ca* 70°C. In the present modification the α'-relaxation appeared at *ca* 40°C. The results indicate that PEP segments in the former system are restricted more than those in the latter. The restriction would be based on the chemical reaction of carboxyl or hydroxyl terminated units of the polyesters and epoxy groups of DGEBA. Then the extent of chemical incorporation of the polyesters into the epoxy matrix would be far less in the DDS curing system. But the incorporation into the matrix could not be neglected, because the dispersed particles size is far fine, the α-relaxation in the $\tan\delta$ curve shifted towards lower temperature both with increasing polyester content and with decreasing polyester MW, and the new relaxation peak at *ca* 90°C existed. The improvement of the toughness would be partly because of the reinforcement of the matrix by the incorporation of the polyesters in the present system. The maintenance of mechanical properties of the modified resins would be also attributable to the reinforcement of the matrix.

T_g's for the modified resins decreased in the use of lower MW polyesters. T_g's for the higher MW polyester-modified resins were equal or slightly low, compared to that for the parent resin.

CONCLUSION

The polyesters are effective modifiers for improving the toughness of epoxy resins. Their effectiveness were hardly influenced by the polyester structure and depended on polyester MW and content. The toughening mechanism is due to two phase separation structures. Their efficiency as modifiers would be because of three causes; (1) the high extent of dispersion of fine polyester-rich particles, (2) the existence of the new relaxations at *ca* 40, 90°C, and (3) the reinforcement of the matrix itself by the incorporated polyesters. The more suitable compositions for the modification of the epoxy resin were inclusion of 20 wt% of PEP (MW 10,300) or PEPI (10 mol.% IP unit, MW 7400).

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