

Modification of Epoxy Resins with Poly(aryl ether ketone)s

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SYNOPSIS

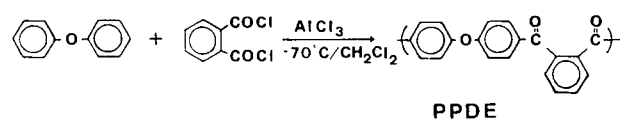
Poly(aryl ether ketone)s were used as modifiers for bisphenol-A diglycidyl ether epoxy resin (AER 331) cured with methyl hexahydrophthalic anhydride. Poly(phthaloyl diphenyl ether) (PPDE), soluble in the uncured epoxy resin without using solvents, was prepared by the Friedel-Crafts reaction of phthaloyl chloride and diphenyl ether. The mechanical, thermal, and dynamic viscoelastic properties of the modified resins with PPDE were examined and compared to the parent resin (AER 331). The fracture toughness, K_{IC} , for the modified resins increased at no expense to their mechanical and thermal properties on 10 wt % addition of PPDE with molecular weights of more than 17,000. The toughening mechanism is discussed based on the morphological and dynamic viscoelastic behaviors 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 resins 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 rubbers¹ or terminally functionalized engineering thermoplastics.² The incorporation of carboxyl-terminated butadiene acrylonitrile rubber (CTBN) increased the fracture toughness of modified resins, but tended to decrease their glass transition temperatures, T_g 's. 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. The use of the epoxide-containing rubbers led to an increase in the fracture toughness, K_{IC} , of the cured resins at a minimal expense of their mechanical and thermal properties.

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. In the preceding paper,⁴ poly[alkylene (iso)phthalate]s have been reported as effective modifiers for epoxy resins. Poly(ethylene phthalate) (PEP) is the most effective modifier and, on 20 wt % addition of PEP with a molecular weight of 7200, the K_{IC} value for the modified resin increased by 150% at no expense to its mechanical properties, though the T_g value decreased slightly.

This paper reports the modification of methyl hexahydrophthalic anhydride (MHHPA)-cured epoxy resins (diglycidyl ether of bisphenol A, DGEBA) with poly(aryl ether ketone)s, which are some of the most interesting engineering thermoplastics because of their good mechanical properties. Poly(phthaloyl diphenyl ether)s (PPDE), soluble in the epoxy resin without using solvents, were prepared as aromatic poly(ether ketone)s by the Friedel-Crafts reaction using phthaloyl chloride as follows:



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The effect of the molecular weight and the amount of PPDE added for the improvement of the cured epoxy resin was examined based on the mechanical and thermal properties of the modified resin.

EXPERIMENTAL

Materials

The epoxy resins used were the liquid bisphenol-A-type epoxy resin (DGEBA) (AER 331, Asahi Chemical Industrial Co., epoxy equivalent weight [EEW] 191). 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 PPDE were determined by gel permeation chromatography (Shimadzu LC-5A instrument) using polystyrene standard calibration. Glass transition temperatures of both PPDE and the cured resins were measured by differential scanning calorimetry (Shimadzu DSC 41M type). The terminal carboxyl contents of PPDE 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. Flexural strength and modulus (JIS K 7203) of cured resins were determined at a crosshead speed of 2 mm/min. Dynamic viscoelastic properties were measured with a Rheometrics RDS-II type (Rheometrics Co.) between -150 and 250°C at a heating speed of $5^{\circ}\text{C}/\text{min}$ at a frequency of 1 Hz. Other measurements are as described previously.⁴

Preparation of poly(phthaloyl diphenyl ether)s (PPDE)

Poly(phthaloyl diphenyl ether)s were prepared by the reaction of phthaloyl chloride and diphenyl ether according to the modified procedure in the patent.⁵

Typical procedures are shown as follows: A 500 mL four-necked flask was charged with diphenyl ether 25.5 g (0.150 mol) and CH_2Cl_2 300 g. After the reaction mixture was cooled to about -70°C , AlCl_3 56.1 g (0.420 mol) was added in portions followed by addition of phthaloyl chloride 39.6 g (0.195

mol) dropwise with stirring. The reaction mixtures were warmed up to -20°C during 1 h and kept for 6 h. Then, the reaction mixtures were stirred while allowing them to rise to room temperature and kept overnight. After refluxing for 30 min, the reaction mixture was poured into ice water. The precipitated polymer was washed with MeOH/acetone (1/1 vol ratio) to remove lower molecular weight products. The ground polymer powder was heated in concentrated HCl aqueous solution to remove the aluminum residue adhered to the polymer. This procedure was carried out several times until the chloride ion could not be detected in the filtrate. The polymer was dried at 80°C in vacuo. Yield 43.2 g (96%); M_{GPC} , 56,300.

Curing Procedure

A mixture of the epoxy resin and PPDE was heated at 120 – 140°C to homogenize. The curing agent, MHHPA, was added into the mixture, which was stirred at 90°C to homogenize and degas, and then an accelerator, benzyldimethylamine (BDMA), was added with gentle stirring to minimize air entrapment for 3 min. The resulting clean mixture was poured into a silicon mold preheated at 100°C . A curing cycle was $85^{\circ}\text{C}/5\text{ h} + 100^{\circ}\text{C}/5\text{ h} + 120^{\circ}\text{C}/5\text{ h} + 150^{\circ}\text{C}/15\text{ h}$. The composition of the parent epoxy resin was as follows: AER 331/MHHPA/BDMA = 100/88/0.5 (wt ratio). The amount (wt %) of PPDE used was calculated based on the epoxy resin.

RESULTS AND DISCUSSION

Preparation and Characterization of Poly(phthaloyl diphenyl ether)s

Table I shows some characteristic properties of poly(phthaloyl diphenyl ether)s (PPDE). Various molecular weights of PPDE were prepared by adjusting the mol ratio of starting materials: diphenyl ether and phthaloyl chloride. PPDE prepared in this study have the higher compatibility owing to their *ortho* linkage compared with conventional aromatic polyether ketones such as poly(ether ether ketone) (PEEK) and were soluble in the epoxy resin (AER 331) without using solvents. Figure 1 shows that PPDE contained small amounts of lower molecular weight products in spite of trying to remove them by washing with MeOH/acetone mixtures. The number-average molecular weight is highly sensitive to the presence of a small number fraction of lower

Table I Characterization of PPDE

	$M_{\text{GPC}}^{\text{a}}$	M_n	M_w	$\frac{M_w}{M_n}$	A.V. ^b (meq/g)	T_m^{c} (°C)
PPDE 1	3,700	4,500	7,500	1.66	0.130	215
PPDE 2	4,300	2,800	4,400	1.57	0.171	242
PPDE 3	9,000	5,300	8,500	1.62	—	230
PPDE 4	17,000	(16,000) ^d	(296,000) ^d	(18.0) ^d	0.148	—
PPDE 5	56,300	7,600	41,100	5.38	0.062	249

^a Obtained from the main peak position of GPC.

^b Terminal carboxyl group content.

^c From DSC: heating rate, 10°C/min.

^d Obtained by another polystyrene calibration (linear).

molecular weight material. Then, the GPC-average molecular weight, obtained from the peak position of the GPC curve, was used as a measure of the molecular weight. The GPC column system (Shimadzu HSG 60, 40, 20, 15, 10) in this study saturated in the region of ca. 40 min. The molecular weight distribution of PPDE of entry no. 4 in Table I was far broader than that of other PPDE, as shown in Figure 1, and its dispersity was obtained using another polystyrene calibration (linear).

Mechanical and Thermal Properties of Modified Epoxy Resins

Preliminary experiments for curing showed that the cured resins tended to separate macroscopically under the usual curing conditions (85°C/5 h + 180°C/15 h). The content of the accelerator, BDMA, was also important, and the use of BDMA 1 wt % based on AER 331 led to the macrophase-separation. This result indicates that the mild curing conditions would be necessary in the PPDE-modification. The most suitable curing conditions are shown in the Experimental section. Table II shows the mechan-

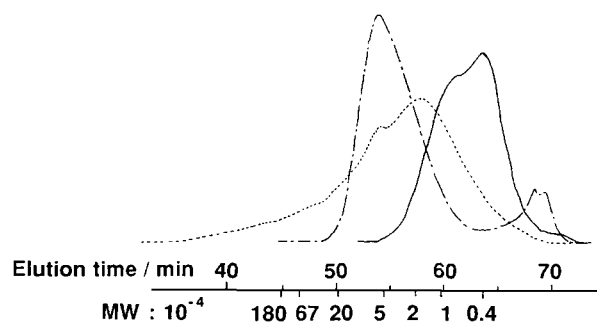


Figure 1 GPC profiles of PPDE: (—) MW, 3,700; (-----) MW, 17,000; (- - -) MW, 56,300.

ical and thermal properties of the PPDE-modified resins. The cured parent epoxy resin was transparent. The cured resins modified with PPDE of molecular weight (MW) 3700 (10 wt %) were also transparent. The cured resin became translucent using PPDE of MW 9000 (10 wt %). The cured resins were transparent in the modification with 10 wt % of PPDE with MW 17,000. This might be due to the higher polydispersity of PPDE with MW 17,000, compared to other PPDE (Table I). The modified resins with higher MW PPDE (MW 56,300) were opaque on addition of 5 or 10 wt %. The addition of PPDE of more than 10 wt % made processing difficult owing to the higher viscosity of uncured sample mixtures. Tensile strength for the cured resins increased with increasing MW of PPDE used. The use of PPDE of MW 56,300 led to a 40% increase in the fracture toughness, K_{IC} , for the modified resin at no expense to its mechanical properties. Figure 2 shows the mechanical properties of the PPDE (MW 56,300)-modified resins as a function of concentration of PPDE. It is interesting that the fracture toughness increased considerably on addition of 10 wt % of PPDE. This result corresponds to morphological and dynamic viscoelastic behaviors (Figs. 3 and 4). On addition of 10 wt % of PPDE, the mechanical strength for the cured resin has a somewhat larger standard deviation, perhaps due to the heterogeneity of the cured resin, as shown below in its morphological examination.

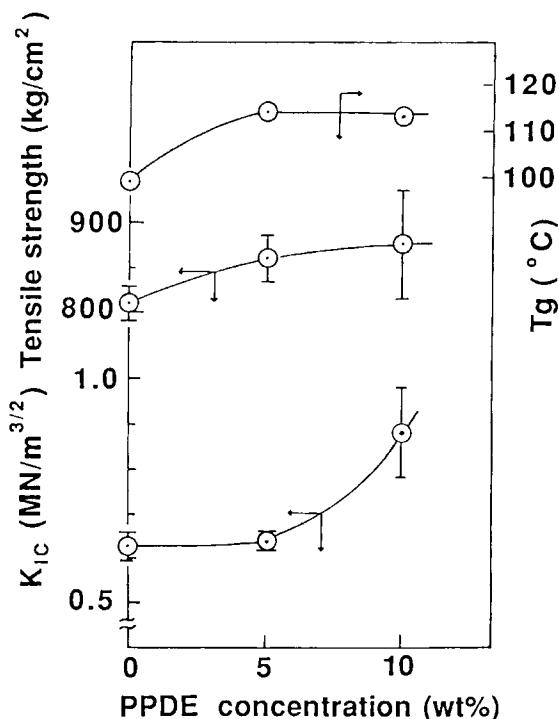
The modification of the cured resins with PPDE (10 wt %) resulted in an increase in the glass transition temperature, T_g 's, even though the MWs of the PPDE used were low. This can be explained as being due to the reinforcement of the parent epoxy matrix itself by incorporation of PPDE. Two T_g 's were observed in the modification with PPDE of MW 56,300 (10 wt %). It is thought that the lower

Table II Mechanical Properties of Cured Epoxy Resins

	Composition (epoxy/PPDE)					
	100/0	90/10	90/10	90/10	90/10	90/10
	Molecular Weight of PPDE					
	3700	4300	9000	17,000	56,300	
Tensile strength (kgf/cm ²)	810 ± 18	722 ± 48	657 ± 56	802 ± 69	846 ± 23	874 ± 62
Elongation at break (%)	5.6 ± 0.4	3.4 ± 0.5	2.9 ± 0.4	3.8 ± 0.4	5.2 ± 0.5	4.9 ± 0.9
Tensile modulus (kgf/mm ²)	297 ± 11	289 ± 15	305 ± 4	301 ± 13	310 ± 12	299 ± 9
<i>n</i> ^a	8	8	8	8	7	9
Flexural strength (kgf/mm ²)	14.3 ± 0.3	11.9 ± 1.5	11.9 ± 2.3	—	15.2 ± 0.2	12.0 ± 2.5
Flexural modulus (kgf/mm ²)	342 ± 11	356 ± 9	354 ± 6	—	357 ± 7	358 ± 9
<i>n</i> ^a	9	8	8	—	5	6
<i>K</i> _{IC} (MN/m ^{3/2})	0.63 ± 0.03	0.63 ± 0.04	0.67 ± 0.07	0.71 ± 0.05	0.71 ± 0.05	0.88 ± 0.10
<i>n</i> ^a	8	8	5	5	7	6
<i>T</i> _g (°C) ^b	99	120	115	111	111	113, 164
Transparency of cured resin	Transparent	Transparent	Transparent	Translucent	Transparent	Opaque

^a Specimen number.^b From DSC: heating rate, 10°C/min.

*T*_g value (113°C) would be based on the epoxy-rich matrix, and the higher one (164°C), on the PPDE-rich phase, considering both DSC results of the cured parent resin and PPDE and a morphology of the modified resin [Fig. 4(c)].

**Figure 2** Effect of PPDE concentration on the mechanical properties of cured epoxy resins.

The solubility parameter (SP) is a measure for compatibility. The SP value (12.15) of PPDE is larger than that (10.60) of the uncured parent epoxy resin,[†] but the phase-separation in the curing with the acid anhydride, MHHPA, was depressed owing to the chemical bonding of terminal carboxyl groups of PPDE and the epoxy matrix or the curing agent.

Morphologies of the Modified Resins

Figures 3 and 4 show the scanning electron microscopy (SEM) of the fracture surface of the PPDE-modified resins. The unmodified resin has only one phase, and the surface is smooth and featureless up to a magnification of 20,000 [Fig. 3(a)]. The fracture surface for the cured resin modified with 10 wt % of PPDE (MW 3700) was slightly rough, but no domain existed [Fig. 3(b)]. The fracture surface for the modified resin with 10 wt % of moderate MW PPDE (MW 9000) was more rough than that with PPDE of MW 17,000, which corresponds to the transparency of the cured resin [Fig. 3(c) and (d)]. The morphology of the fracture surface for the modification with higher MW PPDE (MW 56,300) provided interesting information on the microphase structure of the cured resin. The use of 5 wt % of PPDE (MW 56,300) indicates the existence of somewhat undefined particles less than 0.5 μm in diameter [Figs. 4(a) and (b)]. The use of 10 wt %

[†] Values calculated by Fedors' method (see Ref. 6).

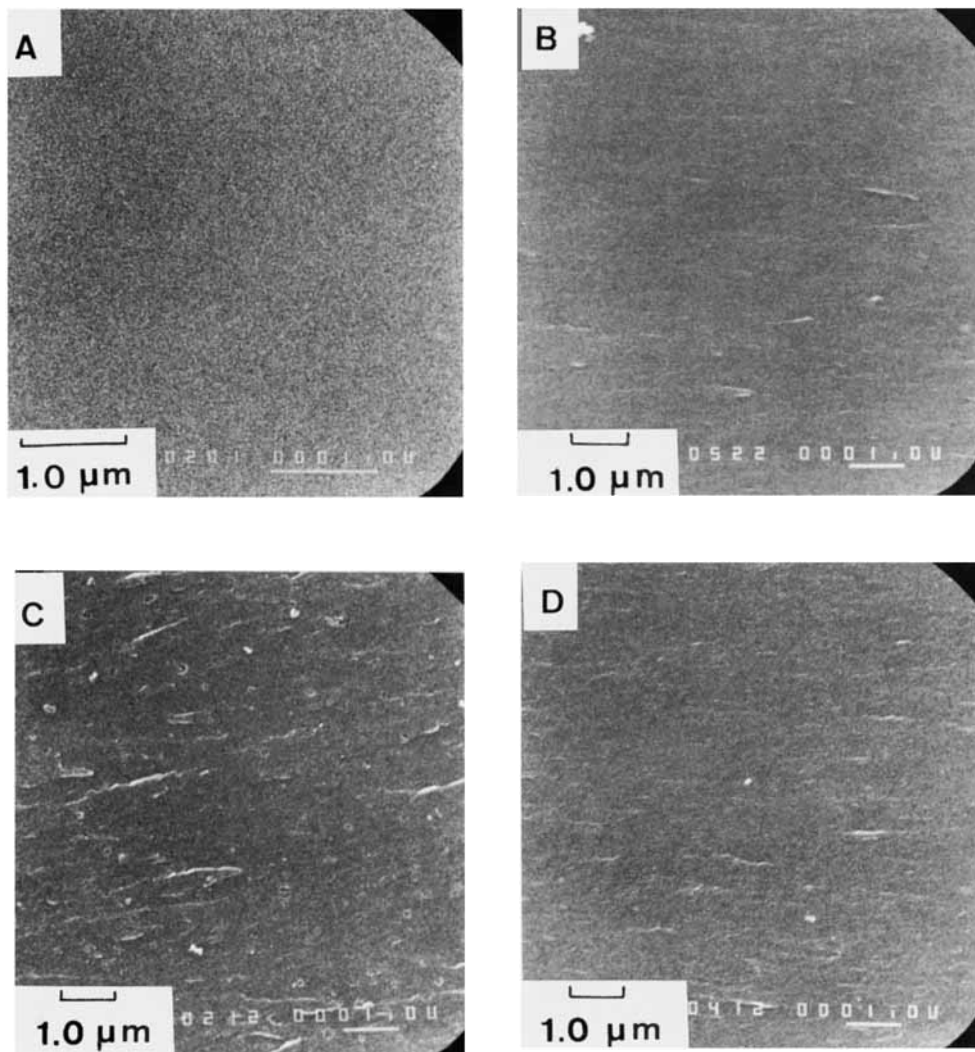


Figure 3 SEMs of fracture surfaces for cured resins modified with 10 wt % of PPDE: (a) control; (b) MW, 3700; (c) MW, 9000; (d) MW, 17,000.

of PPDE (MW 56,300) led to a drastic change in the morphology of the fracture surface. The fracture surface for the modified resin with 10 wt % of PPDE (MW 56,300) indicates a cocontinuous two-phase separation structure induced by a spinodal decomposition [Fig. 4(c)]. It is thought that the dark phase is epoxy-rich, and the light one, PPDE-rich, considering the morphology of the modified resin with 5 wt % of PPDE [Fig. 4(a)]. The volume fraction (0.17) of the light phase is much larger than is the weight fraction (0.10) of the PPDE added in the modification system. This result indicates that the epoxy resin is incorporated into the PPDE-rich phase to a considerable extent. Such behaviors are observed in detail by SEM at higher magnification. Figure 4(d) shows the SEM for the PPDE (MW

56,300) 10 wt % addition system at higher magnification ($\times 540$), where the dark, epoxy-rich phase is smooth and featureless, similar to the parent epoxy resin, and the light one separates microscopically. This phase-separation may be perhaps due to the decrease in the effectiveness of terminal groups for compatibilization in the modification with higher MW PPDE.

Dynamic Mechanical Properties of the Modified Resins

Dynamic mechanical properties can give information on the microstructure of cured resins. Figures 5 and 6 show the temperature dependence of storage

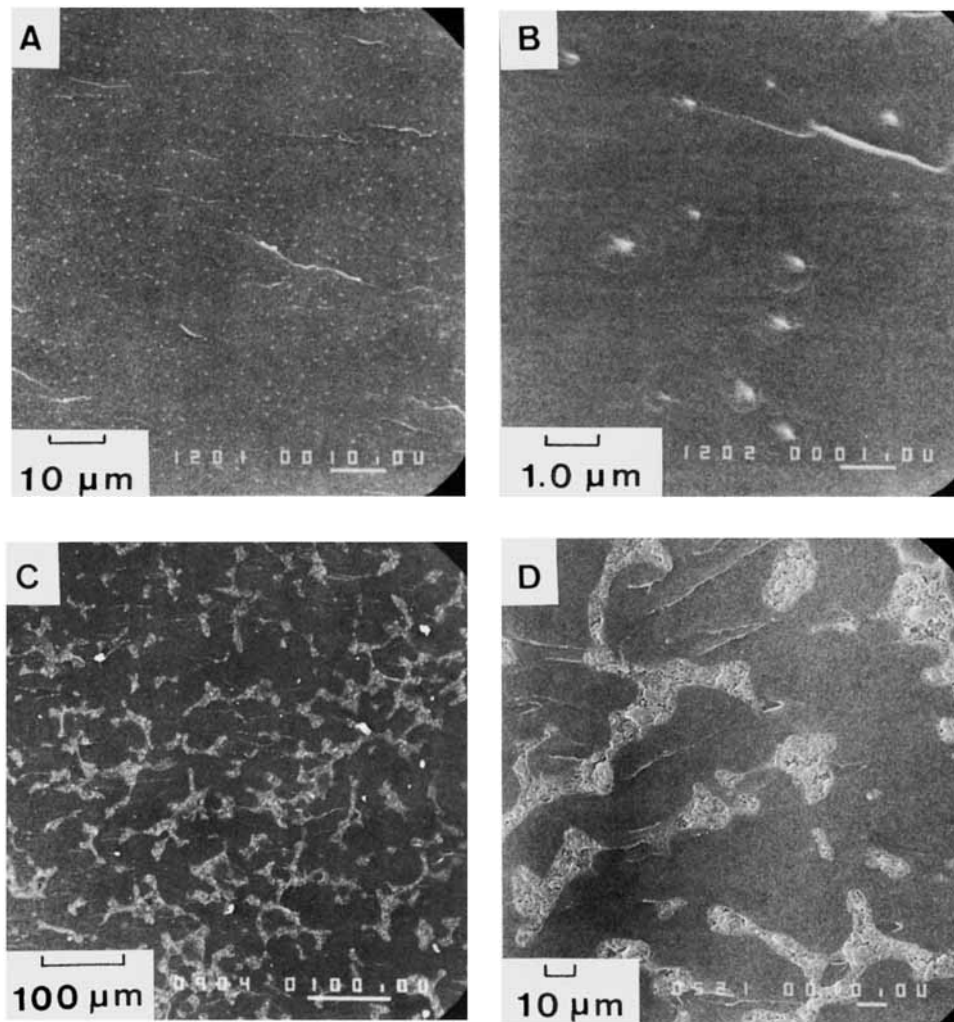


Figure 4 SEMs of fracture surfaces for cured resins modified with PPDE of MW 56,300: (a) and (b), 5 wt % addition; (c) and (d), 10 wt % addition.

moduli, G' , and tangent delta curves. The α -relaxation peak in the $\tan \delta$ curves for the resins modified with 10 wt % of PPDE (MW 17,000) became much broader than that for the parent epoxy resin, though the peak position of the α -relaxation peak for the former hardly changed, compared to that for the latter (Fig. 5). Further, two shoulders (ca. 95 and 185°C) were observed in the $\tan \delta$ curve of the former. The storage modulus increased over the temperature range lower than the α -relaxation, compared to the parent epoxy resin. On addition of 5 wt % of PPDE with MW 56,300, the α -relaxation peak of the $\tan \delta$ curve became slightly broader, compared to the parent epoxy resin (Fig. 6). On addition of PPDE 10 wt % (MW 56,300), dynamic viscoelastic properties change significantly. The α -relaxation peak position in the $\tan \delta$ curve was sim-

ilar to that for the parent epoxy resin, but a new higher temperature peak appeared at ca. 190°C. This result indicates the existence of the phase-separation for the cured resin and corresponds to the morphological result and thermal behavior for the cured resin [Fig. 4(c) and (d)]. The storage moduli increased with an increase in the PPDE concentration over the temperature range lower than the α -relaxation.

Toughening Mechanism

It is well known that the terminally modified butadiene acrylonitrile rubbers such as CTBN are effective modifiers for the epoxy resins and that the two-phase structure and its interfacial bonding are important to decrease the brittleness of the epoxy

resin. In such a modification system, the elastomer particles with an average size of a few microns were dispersed in the epoxy matrix and the interfaces between the matrix and the particles were partly linked by covalent-bonding. In the effective modification system, the toughening mechanism can be explained by the fracture energy dissipation due to the delocalized plastic deformation around elastomer particles that serve as stress concentrators.

Such a toughening mechanism has also been shown in the modification with the pendant epoxy-containing acrylic elastomers such as copolymers containing BA and VBGE or terpolymers composed of BA, VBGE, and St or AN.³

In the modification with engineering thermoplastics, the diameter and volume fraction of domains are less than those in the reactive rubber modification system. For example, there are dispersed particles of less than 1 μm in diameter in the modification with amine-terminated polyether sulfone.² In the modification with such engineering thermoplastics, the reinforcement of the matrix itself is more important to reduce the brittleness of the epoxy resins. It has already been reported that the epoxy matrix itself was reinforced considerably by the incorporated polyesters in the modification with aromatic polyesters such as poly(butylene phthalate) (PBP) and that the fracture toughness

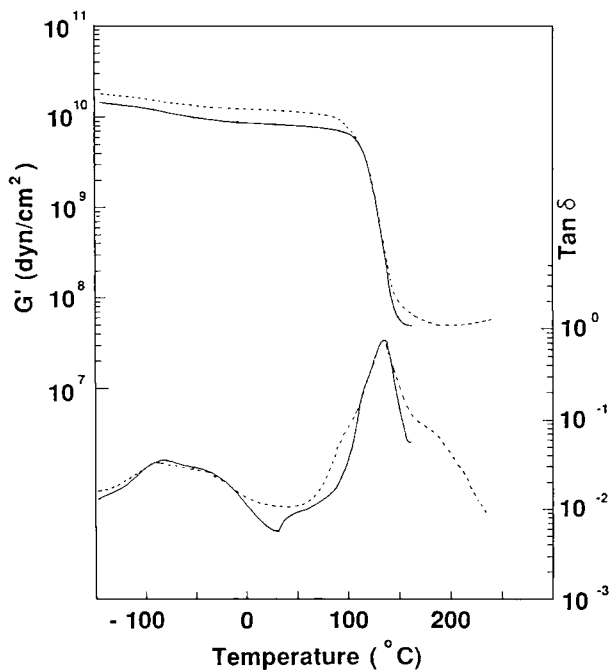


Figure 5 Dynamic viscoelastic analysis for the cured resin: (—) control; (----) PPDE (MW 17,000) 10 wt % addition.

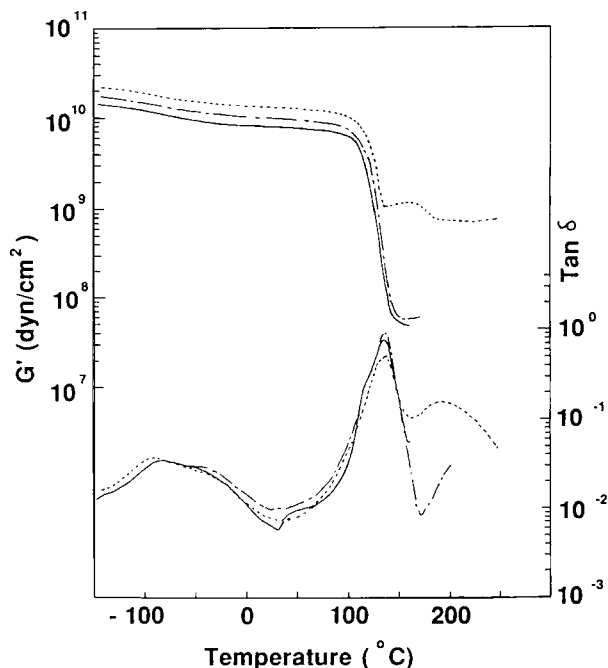


Figure 6 Dynamic viscoelastic analysis for the cured resin modified with PPDE (MW 56,300): (—) control; (----) 5 wt % addition; (-----) 10 wt % addition.

increased at no expense to its mechanical properties of the cured resin.⁴

Morphological and dynamic mechanical behaviors indicate that there is high compatibility between the parent epoxy resin and PPDE having MW less than 17,000. The toughening mechanism in these PPDE modification systems is similar to that with PBP. The fracture surface for the modified resin with 10 wt % of higher MW PPDE (MW 56,300) resulted in the cocontinuous two-phase structure, where the cured resin was improved with no sacrifice to its mechanical and thermal properties, compared to the parent epoxy resin. Recently, such microphase structures for the cured epoxy resin have been reported in the modification with poly(aryl ether sulfone)s (PES); the PES-modified epoxy resin has a connected-global structure by a spinodal decomposition, dependent on the curing conditions, and exhibits higher adhesive strength than does the unmodified resin.⁷ In the present PPDE modification system, the modified resin with 10 wt % of PPDE (MW 56,300) has the cocontinuous two-phase structure and its K_{IC} value increased by 40% with a slight increase in tensile strength and a 14°C increase in T_g . It is believed that this improvement to mechanical and thermal properties resulted from the cocontinuous structure by spinodal decomposition.

In conclusion, poly(phthaloyl diphenyl ether)s

(PPDE) were effective as modifiers for the epoxy resin. Modification of the cured epoxy resin with PPDE led to an increase in the fracture toughness of the cured resin at no expense to its mechanical properties. The most suitable composition for modification of the epoxy resin was inclusion of 10 wt % of PPDE (MW 56,300), which resulted in a 40% increase in the fracture toughness, K_{IC} , at no expense to the mechanical strength of cured resin, where the toughening mechanism of cured resin is due mainly to the cocontinuous structure.

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