

Modification of Bismaleimide Resin by Poly(ethylene phthalate-co-ethylene terephthalate), Poly(ethylene phthalate-co-ethylene 4,4'-biphenyl dicarboxylate), and Poly(ethylene phthalate-co-ethylene 2,6-naphthalene dicarboxylate)

TAKAO IJIMA, HIROSHI ONO, MASAO TOMOI

Department of Applied Chemistry, Faculty of Engineering, Yokohama National University, Tokiwadai 79-5, Hodogaya-ku, Yokohama, 240 Japan

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ABSTRACT: Aromatic polyesters were prepared and used to improve the brittleness of bismaleimide resin, composed of 4,4'-bismaleimidodiphenyl methane and *o,o'*-diallyl bisphenol A (Matrimid 5292 A/B resin). The aromatic polyesters included PEPT [poly(ethylene phthalate-co-ethylene terephthalate)], with 50 mol % of terephthalate, PEPB [poly(ethylene phthalate-co-ethylene 4,4'-biphenyl dicarboxylate)], with 50 mol % of 4,4'-biphenyl dicarboxylate, and PEPN [poly(ethylene phthalate-co-ethylene 2,6-naphthalene dicarboxylate)], with 50 mol % 2,6-naphthalene dicarboxylate unit. The polyesters were effective modifiers for improving the brittleness of the bismaleimide resin. For example, inclusion of 15 wt % PEPT (MW = 9300) led to a 75% increase in fracture toughness, with retention in flexural properties and a slight loss of the glass-transition temperature, compared with the mechanical and thermal properties of the unmodified cured bismaleimide resin. Microstructures of the modified resins were examined by scanning electron microscopy and dynamic viscoelastic analysis. The toughening mechanism was assessed as it related to the morphological and dynamic viscoelastic behaviors of the modified bismaleimide resin system. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 2352–2367, 2001

Key words: bismaleimide resin; modification; poly(ethylene phthalate-co-ethylene terephthalate); poly(ethylene phthalate-co-ethylene 4,4'-biphenyl dicarboxylate); poly(ethylene phthalate-co-ethylene 2,6-naphthalene dicarboxylate); fracture toughness

INTRODUCTION

Addition polyimide resins are among the most important thermosetting polymers and have received attention because of their mechanical properties and their high thermal stability. But they also have the drawbacks of being brittle and

difficult to process. Bismaleimide resins have also been attractive because of good processibility and nonvolatility. A two-component bismaleimide system (Matrimid 5292 A/BTM), composed of 4,4'-bismaleimidodiphenyl methane (BMI) and *o,o'*-diallyl bisphenol A (DBA), has been developed by Ciba Geigy Corp. to improve mechanical properties and processibility.¹ DBA copolymerizes with BMI via an ene reaction during curing. The brittleness of the cured resin is improved, as compared to conventional bismaleimide resins, but its

Correspondence to: T. Iijima (tijima@ynu.ac.jp).

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fracture toughness is not yet sufficient for use as the composite matrix.

The toughness of epoxy resins has been increased by blending with reactive liquid rubbers such as carboxyl-terminated butadiene-acrylonitrile rubbers (CTBN).² Engineering thermoplastics are interesting materials as modifiers for epoxy resins from the viewpoint of maintaining mechanical and thermal properties. Recently, various types of ductile thermoplastics, including polysulfone, poly(ether imide) and poly(ether ketone), have been used as alternatives to reactive elastomers for improving the brittleness of thermosets such as epoxy and bismaleimide resins. Advances in modification of the bismaleimide resin have previously been reviewed.³⁻⁵

Modification of the bismaleimide resin (the Matrimid 5292 system) has been carried out on the basis of information on the toughening of thermosetting resins by thermoplastics in our laboratory⁶⁻¹⁶ In previous articles we have reported that PEP [poly(ethylene phthalate)] and related copolyesters are effective modifiers of epoxy resins.^{6,12} PBP [poly(butylene phthalate)] and related polyesters were also effective as modifiers for epoxies.¹⁷ More recently, we have reported that PEP, PPP [poly(propylene phthalate)], and PBP are effective modifiers for the bismaleimide resin.^{18,19} And, most recently, PEP and related copolyesters have been examined as modifiers for the cyanate ester resin.²⁰

This article reports on modification of the bismaleimide resin (the Matrimid 5292 A/B system) by aromatic polyesters containing rigid groups in the backbone. These aromatic polyesters include PEPT [poly(ethylene phthalate-co-ethylene terephthalate), 50 mol % of the terephthalate (TP) unit], PEPB [poly(ethylene phthalate-co-ethylene-4,4'-biphenyl dicarboxylate, 50 mol % of the 4,4'-biphenyl dicarboxylate (BD) unit], and PEPN [poly(ethylene phthalate-co-ethylene 2,6-naphthalene dicarboxylate, 50 mol % of the 2,6-naphthalene dicarboxylate (ND) unit]. The effects of structure, molecular weight, and amount of polyesters used on the toughness of the cured resins were examined.

EXPERIMENTAL

Materials

Matrimid 5292 A/B, a commercially available bismaleimide resin composed of BMI and DBA (Ciba

Geigy Corp., Fribourg, Switzerland), was used. The aromatic polyesters were prepared by reacting 1,2-ethanediol with aromatic dicarboxylic acids (phthalic anhydride, terephthalic acid, 4,4'-biphenyl dicarboxylic acid and 2,6-naphthalene dicarboxylic acid), as reported previously.⁶ Other reagents were used as received.

Measurements

¹H-NMR spectra were recorded on a 90-MHz instrument (JEOL JNM-9MX 90, Tokyo, Japan) at 60°C using CDCl₃ as solvent and tetramethylsilane as internal standard. The molecular weights of the polyesters were measured by gel permeation chromatography (Shimadzu LC-5A instrument, Kyoto, Japan) using polystyrene standards. The terminal carboxyl contents of the polyesters were analyzed by titration with an 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 crosshead speed of 2 mm/min (JIS K7203). Fracture toughness, K_{IC} , was measured in a 3-point bent geometry at a crosshead speed of 1 mm/min (ASTM E-399). The onset glass-transition temperature (T_g) of the polyester was measured by differential scanning calorimetry (41M or 60 Shimadzu DSC) at a heating speed of 10°C/min under nitrogen. The T_g of the cured resin was obtained by dynamic viscoelastic analysis. Dynamic viscoelastic analysis was performed with a Rheometrics RDS-II (Rheometrics Co., Tokyo, Japan) between -50°C and 400°C at a heating speed of 5°C/min at frequency of 1 Hz. Scanning electron micrographs (SEMs) were taken with a combined microanalyzer (JEOL, JXA-8900RL, Tokyo, Japan) using failed specimens in the K_{IC} tests.

Curing Procedure

The polyesters were dissolved into DBA at 140°C without solvents. Then BMI was added to the mixture, which was kept at 140°C to dissolve BMI. The resulting clean mixture was degassed in vacuo at 140°C. Equivalent amounts (1:1) of BMI and DBA were used. The mixture was poured into a mold, preheated at 140°C, to obtain 7-mm-thick plaques. The mold consisted of one pair of upright metal-clip-held glass plates spaced by a U-shaped silicon rubber stick. The amount

Table I Characterization of Aromatic Polyesters

Entry No	Polyester ^a Composition	M_{GPC}^b (10^3)	M_n^b (10^3)	M_w/M_n	T_g^c (°C)	Acid Content (meq/g)
PEPT 16	TP 52	6.1	4.2	1.6	43	—
2	52	9.3	5.7	1.8	—	0.022
14	53	11.7	6.7	1.8	47	—
15	53	16.1	9.4	1.8	—	—
10	53	23.7	13.4	2.0	55	0.008
PEPB 6	BD 47	8.4	5.0	1.8	—	—
7	48	12.3	6.8	1.9	65	—
3	48	13.8	8.1	1.8	67	0.018
5	49	23.4	12.0	2.0	67	0.011
PEPN 10	ND 49	6.1	4.4	1.5	—	—
4	50	16.1	9.4	1.7	—	—
7	52	22.3	12.7	1.8	46	0.010
5	52	29.4	18.5	1.7	51	0.011

^a TP, terephthalate unit; BD, 4,4'-biphenyl dicarboxylate unit; ND, 2,6-naphthalene dicarboxylate unit mol %.

^b By GPC.

^c By DSC.

(wt %) of the modifier was calculated based on the matrix resin. The curing cycle was: 160°C/5 h + 180°C/1 h + 200°C/5 h + 250°C/6 h. After curing, the oven temperature was decreased at a cooling rate of 25°C/h from 250°C to 50°C. It is noteworthy that the curing conditions in this study were slightly different from those (160°C/3 h + 180°C/1 h + 200°C/2 h + 250°C/6 h) in the PEP, PPP, and PBP modification systems^{18,19} because the use of the latter conditions led to macrophase separation of the PEPT-modified resins.

Transesterification of Polyesters with DBA

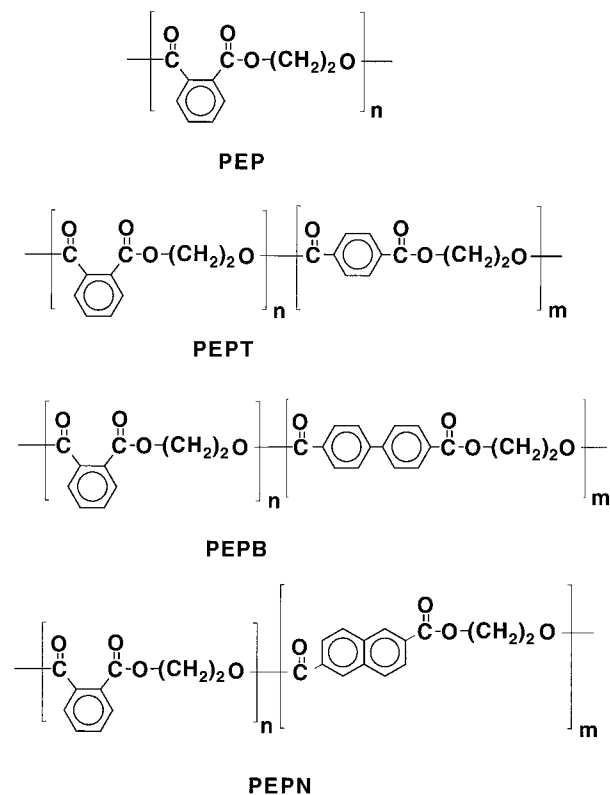
Transesterification of the polyesters and DBA during curing was examined as follows. The polyesters were dissolved into DBA at 140°C at a weight ratio of 20 wt % polyester inclusion, and the reaction was carried out under the appropriate reaction conditions. After the conclusion of the reaction, the reaction mixtures were diluted with CHCl₃, and a resulting polymer was isolated using methanol as precipitant. The polymer was purified twice by reprecipitation with CHCl₃-methanol and dried *in vacuo* at 80°C. The resulting polymer was analyzed by ¹H-NMR spectroscopy (60°C in CDCl₃) and gel permeation chromatography (GPC).

RESULTS AND DISCUSSION

Characterization of Aromatic Polyesters

In this study aromatic polyesters of various molecular weights were prepared in quantitative

yield by polycondensation of 1,2-ethanediol and aromatic dicarboxylic acids, as reported previously.⁶ Table I describes some characteristic properties of aromatic polyesters, and the structures of the polyesters used are shown in Scheme 1. All



Scheme 1 Structure of aromatic polyesters.

the polyesters were white solids and dissolved into DBA without solvents. The GPC average molecular weight (M_{GPC}), based on the peak position in the GPC curve, was used as a measure of the molecular weight (MW) in this and previous studies^{6,12,17-19} because the number-average molecular weight is highly sensitive to the presence of a small amount of materials of a lower molecular weight.

Mechanical and Thermal Properties of Modified Bismaleimide Resins

The unmodified bismaleimide resin was transparent, as reported previously.¹⁵ The transparency of the modified resins depended on the modifier structure, the MW, and the content. In the modification of the bismaleimide resin with PEPT of a low MW (6100), the modified resin was transparent on inclusion of 15 wt % PEPT. When using 10 wt % PEPT (MW = 9300), the modified resin was transparent, whereas the modified resins became translucent on inclusion of 15 wt % of the same polyester and opaque on inclusion of 20 wt %. The modified resin was opaque on inclusion of 15 wt % PEPT (MW = 11,700). When using PEPB, all the modified resins became opaque except for inclusion of 5 wt % PEPB (MW = 8400), in which the modified resin was transparent. In the PEPN modification system all the modified bismaleimide resins were transparent. These results indicate that miscibility of the aromatic polyesters with the bismaleimide resin remarkably depends on the structure of backbone of the polyesters.

Figure 1 shows the mechanical and thermal properties of the modified resins as a function of concentration of PEPT (MW = 9300). For comparative purposes, the results for PEP modification are also shown with the T_g values obtained by dynamic viscoelastic analysis (the T_g values obtained by DSC were shown in the previous article).¹⁸ The K_{IC} for the modified resins increased with increasing PEPT concentration up to 15 wt % addition and then leveled off; the K_{IC} increased 75% on 15 wt % addition. The K_{IC} value (1.16 MPam^{1/2}) for the PEPT-modified resin on 15 wt % addition is comparable to that (1.24 MPam^{1/2}) for the PEP-modified resin on 20 wt % inclusion. Flexural strength for the modified resins was equal to those for the unmodified and PEP-modified resins. Flexural moduli for the modified resins decreased slightly with increasing modifier concentration. The T_g values for the modified resins decreased slightly. It is noteworthy that the

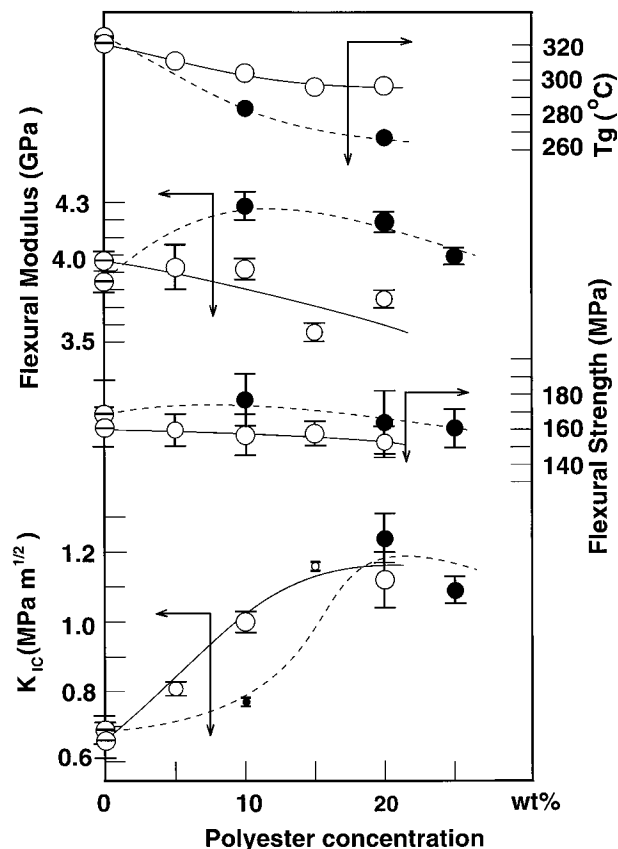


Figure 1 Physical properties of modified resins as a function of polyester concentration: (\ominus) control; (\circ) PEPT (MW = 9300); (\bullet) PEP (MW = 18,200).¹⁸

extent of the decrease in the T_g values for the PEPT-modified resins was far lower than that of the PEP-modified materials.¹⁸

Figure 2 shows the dependence of physical properties of the modified resin on the PEPT MW on 15 or 20 wt % inclusion. The K_{IC} values for the modified resins increased with increasing PEPT MW on 15 wt % inclusion. Flexural strength and modulus for the modified resins was equal to those for the unmodified resins. On 20 wt % inclusion the K_{IC} for the modified resin depended considerably on the molecular weight of the PEPT: PEPT with a molecular weight of 9300 was effective, while the K_{IC} decreased in the modification by PEPT of a higher molecular weight. Especially, when using 20 wt % PEPT (MW = 23,700), the K_{IC} for the modified resin decreased abruptly because of macrophase separation of the modifier, as shown later. Flexural strength and modulus for the resin modified by 20 wt % PEPT decreased with increasing molecular weight of the PEPT. The T_g values for the modi-

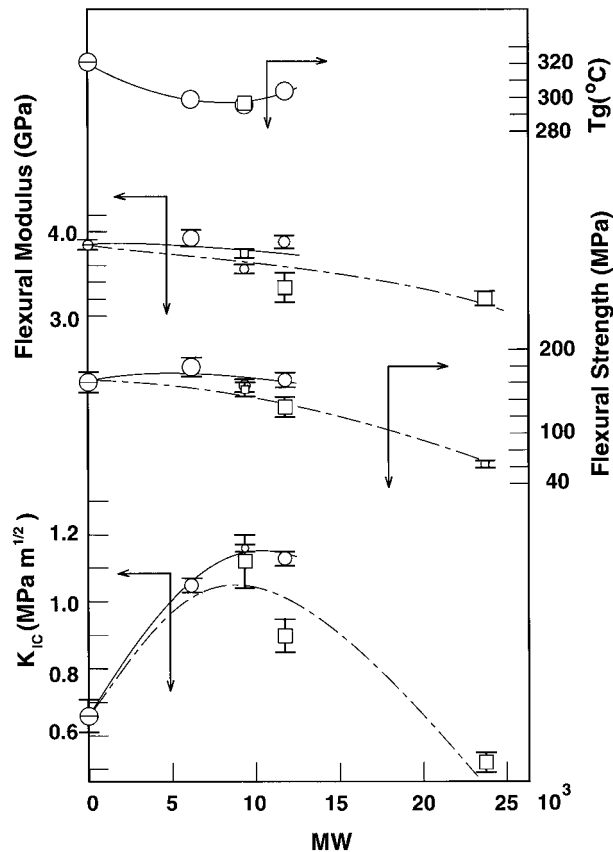


Figure 2 Dependence of physical properties of modified resins on polyester molecular weight: (⊖) control; (○) addition of 15% wt PEPT; (□) addition of 20% wt PEPT.

fied resins decreased slightly as compared with that for the unmodified resin.

Figure 3 shows the mechanical and thermal properties of the modified resins as a function of PEPB and PEPN concentration. The K_{IC} for the resin modified by PEPB with a MW of 8400 increased with increasing PEPB concentration up to 10 wt % and then decreased; macrophase separation occurred on 20 wt % inclusion of the same modifier. The use of PEPB with a higher MW (12,300) resulted in a 75% increase in K_{IC} on 15 wt % inclusion, while the modified resin phase-separated macroscopically on 20 wt % inclusion, and its K_{IC} value decreased suddenly. Flexural strength for the PEPB-modified resin was comparable up to 15 wt % addition of PEPB (MW = 8400 or 12,300) to that for the unmodified resin and decreased abruptly on 20 wt % addition. Flexural moduli for the resins modified by PEPB with a MW of 8400 were also comparable up to 15 wt % addition to the value for the parent resin but

decreased remarkably on 20 wt % inclusion. The flexural modulus for the resin modified by PEPB with a MW of 12,300 decreased gradually with increasing PEPB concentration. When using 20 wt % PEPN (MW = 16,100), the K_{IC} for the modified resin increased by 70%, and its flexural properties were undeteriorated, as compared with those for the parent resin. The T_g values for the modified resins were slightly lower in every case than that for the unmodified resin.

Figure 4 shows the dependence of the physical properties of the modified resin on the molecular weights of PEPB and PEPN. When using 10 wt % PEPB, the K_{IC} values for the modified resins increased with increasing PEPB molecular weight, and their flexural properties did not deteriorate, as compared with those for the unmodified resins; the K_{IC} for the resin modified by PEPB (MW

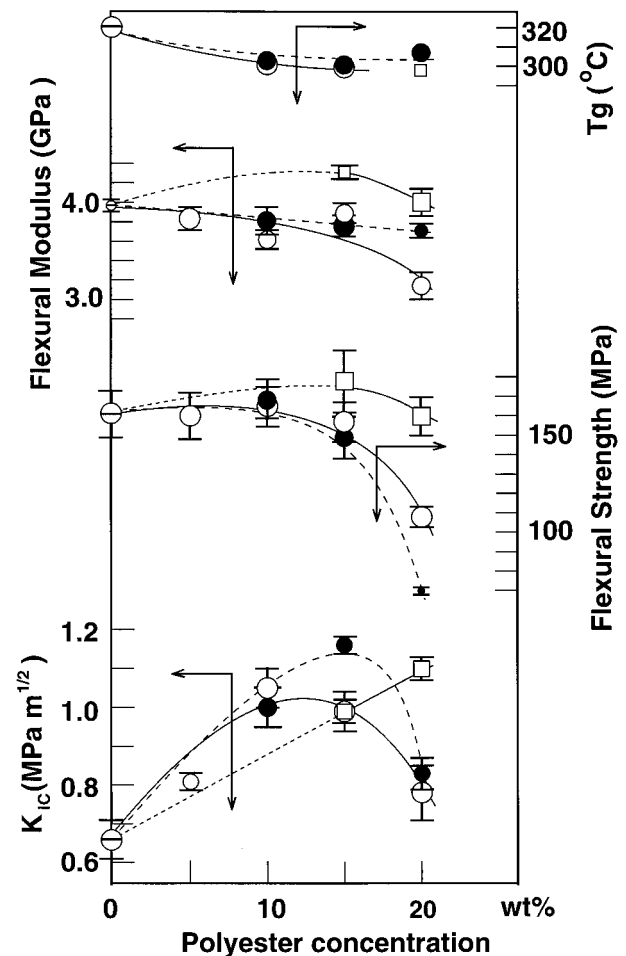


Figure 3 Physical properties of modified resins as a function of polyester concentration: (⊖) control; (○) PEPB (MW = 8400); (●) PEPB (MW = 12,300); and (□) PEPN (MW = 16,100).

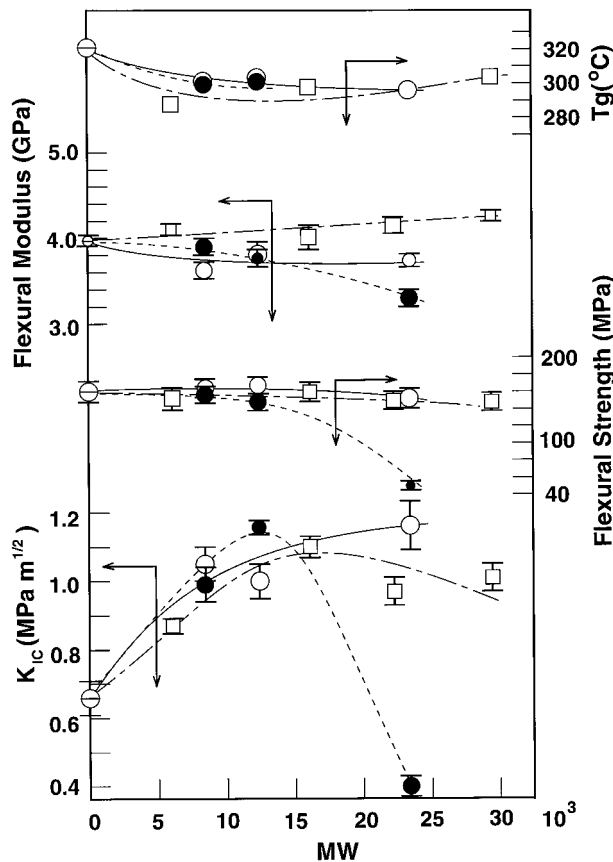


Figure 4 Dependence of physical properties of modified resins on polyester molecular weight: (○) control; (○) addition of 10% wt PEPB; (●) addition of 15% wt PEPB; and (□) addition of 20% wt PEPN.

= 23,400) increased 75%. On 15 wt % inclusion the K_{IC} values for the PEPB-modified resins depended on the molecular weight of the PEPB—the use of PEPB with a molecular weight of 12,300 led to a 75% increase in K_{IC} , but there was an extreme decrease in K_{IC} when using higher-molecular-weight PEPB (MW = 23,400) because of macrophase separation. Flexural strength and modulus also decreased on inclusion of 15 wt % PEPB (MW = 23,400). In modification with 20 wt % PEPN, the K_{IC} for the modified resin increased with increasing molecular weight of the PEPN and then decreased. The flexural properties of the PEPN-modified resin were maintained, independent of the PEPN MW. The T_g values for the modified resins decreased slightly in every case.

Table II shows the representative results for the modification of the bismaleimide resin using the aromatic polyesters. All the polyesters used in this study were effective modifiers for bismaleimide. It was found that the most suitable composi-

tions for toughening bismaleimide resin are PEPT Nos. BT 17 and 14 (15–20 wt %, MW = 9300), PEPB No. BB 18 (15 wt %, MW = 12,300), PEPB No. BB 17 (10 wt %, MW = 23,400), and PEPN No. BN 9 (20 wt %, MW = 16,100). The toughening efficiency of these polyesters is comparable to PEP: the most suitable composition in the PEP modification was 20 wt % inclusion (MW = 18,200), with the K_{IC} for the modified resin increasing 80% with no loss of mechanical properties and a decrease in T_g .¹⁸

Microstructures of Modified Bismaleimide Resins

The morphologies of the cured resins were investigated by scanning electron micrographs (SEMs). The unmodified cured Matrimid resin had only one phase, as reported previously.¹⁵ Figure 5 shows SEMs for the PEPT-modified resins. When using 15 wt % PEPT (MW = 9300), the fracture surface was rough because of the increase in the plastic deformation of the crack tip in the process of the crack propagation, and the modified resin had a particulate structure with somewhat irregular, fine PEPT-rich particles (less than 1 μm in diameter) dispersed in the matrix [Fig. 5(a)]. The morphology of the modified resin became slightly clear by etching in CHCl_3 for 3 days; in Figure 5(b) very fine etched-out holes can be observed, indicating the particulate structure of the modified resin. On 20 wt % inclusion of the same polyester, fine holes can also be observed in the etched fracture surface, with the number of holes increasing and the sizes of those holes increasing slightly [Fig. 5(c)]. When using 20 wt % of the same polyester at a higher molecular weight (23,700), the modified resin has a phase-inverted structure and bismaleimide-rich particles with diameters of more than 1 μm can be observed [Fig. 5(d)].

Figure 6 shows SEMs for the PEPB-modified resins. When using 10 wt % PEPB (MW = 8400), the fracture surface of the modified resin was also rough, but its morphology was obscure [Fig. 6(a)]. The etched fracture surface revealed a particulate structure having fine holes dispersed in the matrix [Fig. 6(b)]. The fracture surface of the modified resin on 20 wt % inclusion of the same modifier was rougher than that on 10 wt % inclusion [Fig. 6(c)], while the etched surface of the former resin differed from that of the latter material [Fig. 6(d)]: the former resin phase-separated macroscopically during curing. The flat matrix and irregular shaped rugged modifier-rich phase can be

Table II Physical Properties of Modified Bismaleimide Resins

Entry No	Polyester				Flexural Properties					
	No ^a	Composition (mol %)	MW (10 ³)	Content (wt %)	K_{IC}^b (MPa · m ^{1/2})	n^c	Strength ^b (MPa)	Modulus ^b (GPa)	n^c	T_g^d (°C)
Control			—	—	0.66 ± 0.05	7	161 ± 12	3.97 ± 0.05	11	321
<i>PEPT series</i>		TP unit								
BT20	PEPT16	52	6.1	15	1.05 ± 0.02	6	180 ± 11	4.13 ± 0.09	5	299
17	PEPT 2	52	9.3	15	1.16 ± 0.01	7	158 ± 7	3.56 ± 0.05	5	296
14	PEPT 2	52	9.3	20	1.12 ± 0.08	5	153 ± 9	3.75 ± 0.04	5	297
21	PEPT14	53	11.7	15	1.13 ± 0.02	7	162 ± 9	3.89 ± 0.07	5	304
15	PEPT10	53	23.7	20	0.52 ± 0.03	5	63 ± 3	3.21 ± 0.18	5	—
<i>PEPB series</i>		BD unit								
BB 14	PEPB 6	47	8.4	10	1.05 ± 0.05	5	165 ± 10	3.62 ± 0.09	5	301
19	PEPB 7	48	12.3	10	1.00 ± 0.05	6	168 ± 9	3.81 ± 0.14	5	303
18	PEPB 7	48	12.3	15	1.16 ± 0.02	6	149 ± 11	3.76 ± 0.10	4	301
20	PEPB 7	48	12.3	20	0.83 ± 0.04	7	70 ± 1	3.71 ± 0.07	6	307
17	PEPB 5	49	23.4	10	1.16 ± 0.07	7	152 ± 11	3.72 ± 0.07	7	296
<i>PEPN series</i>		ND unit								
BN 10	PEPN 4	50	16.1	15	0.99 ± 0.03	7	178 ± 16	4.31 ± 0.06	5	—
9	PEPN 4	50	16.1	20	1.10 ± 0.03	6	160 ± 10	4.00 ± 0.14	6	298
12	PEPN 5	52	29.4	20	1.01 ± 0.04	6	148 ± 8	4.25 ± 0.06	6	304

^a Entry number in Table 1.^b The ± *x* values show standard deviation.^c Number of specimens tested.^d By Dynamic viscoelastic analysis.

observed in Figure 6(d): the modifier-rich phase is not etched out and looks like a cluster of particles. The use of 15 wt % PEPB (MW = 12,300) led to a particulate structure, and various sizes of holes can be observed: the diameters of the holes are in the range of about 0.1–1 μm [Fig. 6(e)]. When using 20 wt % of the same polyester, the morphology of the modified resin became phase-inverted structure [Fig. 6(f)]. On 10 wt % inclusion, the morphology of the PEPB-modified resin (MW = 23,400) was a cocontinuous phase structure [Fig. 6(g)], in which the PEPB-rich phases could not be removed by etching: part of the PEPB-rich phases remained adhered to the dark flat bismaleimide matrix, and the PEPB-rich phases were clusters of PEPB-rich small particles.

Figure 7 shows SEMs for the PEPN-modified resins. The fracture surfaces of the PEPN 15 wt %-modified resins (MW = 16,100) were rough [Fig. 7(a)]. When using 20 wt % of the same modifier, the fracture surface became rougher and ridgier, but its morphology was obscure [Fig. 7(b)]. The morphology of the modified resin was also obscure on 20 wt % inclusion of PEPN (MW = 29,400) [Fig. 7(c)]. The solvent-etched surfaces were rather obscure but revealed some character-

istic morphology: fine holes of less than 1 μm in diameter were observed in the fracture surface in every case [Fig. 7(d–f)].

Dynamic viscoelastic analysis can provide information on the microstructure of cured resins. Figure 8 shows the storage moduli, G' , and $\tan \delta$ curves for the unmodified and PEPT-modified resins. When using PEPT (MW = 9300), the peak positions of the α -relaxation in the $\tan \delta$ curve shifted toward a lower temperature, its shape becoming considerably broader with increasing PEPT concentration. The magnitude of the $\tan \delta$ curve increased to a considerable extent in that region, from room temperature to the α -relaxation peak temperature, as compared to the dynamic viscoelastic behavior of the cured Matrimid resin. A new relaxation peak (α' -relaxation) appeared at 35°C on 10 wt % inclusion, and the α' -relaxation peak magnitude increased with increasing PEPT concentration. The broadness of the α -relaxation and the increase in the magnitude of the $\tan \delta$ curve above the α' -relaxation temperature indicate a matrix structure that is complex, perhaps because of the incorporation of PEPT into the network by transesterification, as shown later. The appearance of the new α' -relax-

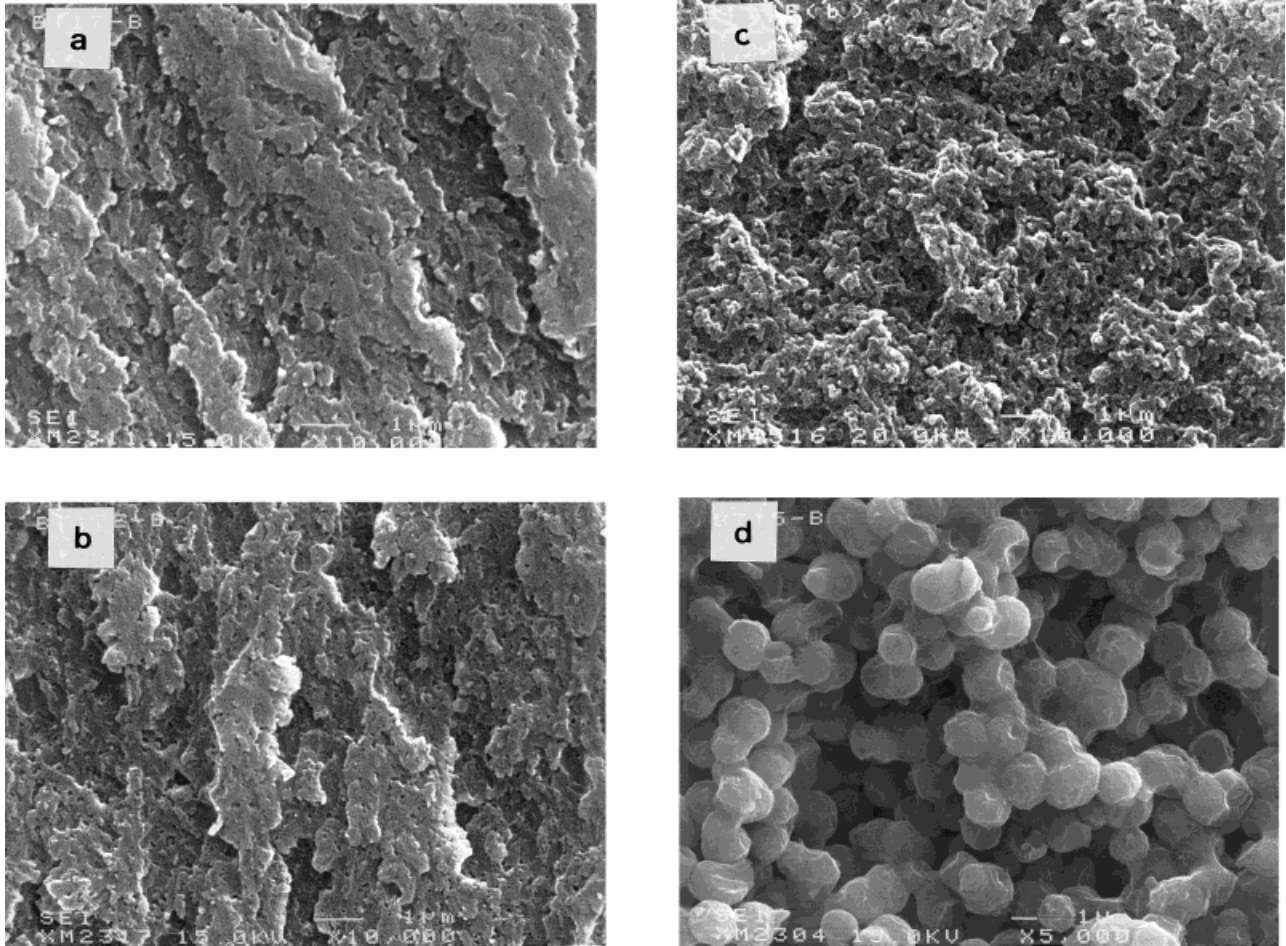


Figure 5 SEMs of fracture surfaces for PEPT-modified resins: (a) addition of 15% wt PEPT (MW = 9300); (b) addition of 15% wt PEPT (MW = 9300) after etching (CHCl_3 , 3 days); (c) addition of 20% wt PEPT (MW = 9300) after etching; and (d) addition of 20% wt PEPT (MW = 23,700).

ation peak in the $\tan \delta$ curve indicates that the modified resin has a phase-separated structure and that the increase in PEPT concentration has led to a greater magnitude of phase separation. The storage moduli at room temperature for the modified resins were smaller than that for the unmodified resin.

Figure 9 shows that on PEPT 15 wt % inclusion, the dynamic viscoelastic behaviors depend on the molecular weight of PEPT. The shift toward a lower temperature of the α -relaxation peak positions, their broadness, and an increase in magnitude of the $\tan \delta$ curve above the α' -relaxation temperature were also observed. The α' -relaxation peak in the $\tan \delta$ curve appeared at about 35°C , and its magnitude increased with increasing molecular weight of the PEPT.

Figure 10 shows the dynamic viscoelastic analyses of the unmodified and PEPB-modified resins

(MW = 12,300). The α -relaxation peak positions hardly changed independent of PEPB concentration, and the broadness of the α -relaxation peak was not significant, as compared with that in the PEPT modification. When using 20 wt % PEPB, the α' -relaxation peak magnitude increased significantly, which corresponds to the macrophase-separated structure of the cured resin [Fig. 6(f)]. The storage moduli at room temperature for the modified resin were smaller than that for the unmodified resin.

Figure 11 shows the storage moduli, G' , and $\tan \delta$ curves for the unmodified and PEPN-modified resins. The dynamic viscoelastic behaviors for the modified resins are similar to those in the PEPT modification (Fig. 9) except for the behavior in the α' -relaxation peak: a shift of the α -relaxation peak position toward a lower temperature, broadness of the α -relaxation peak, and an in-

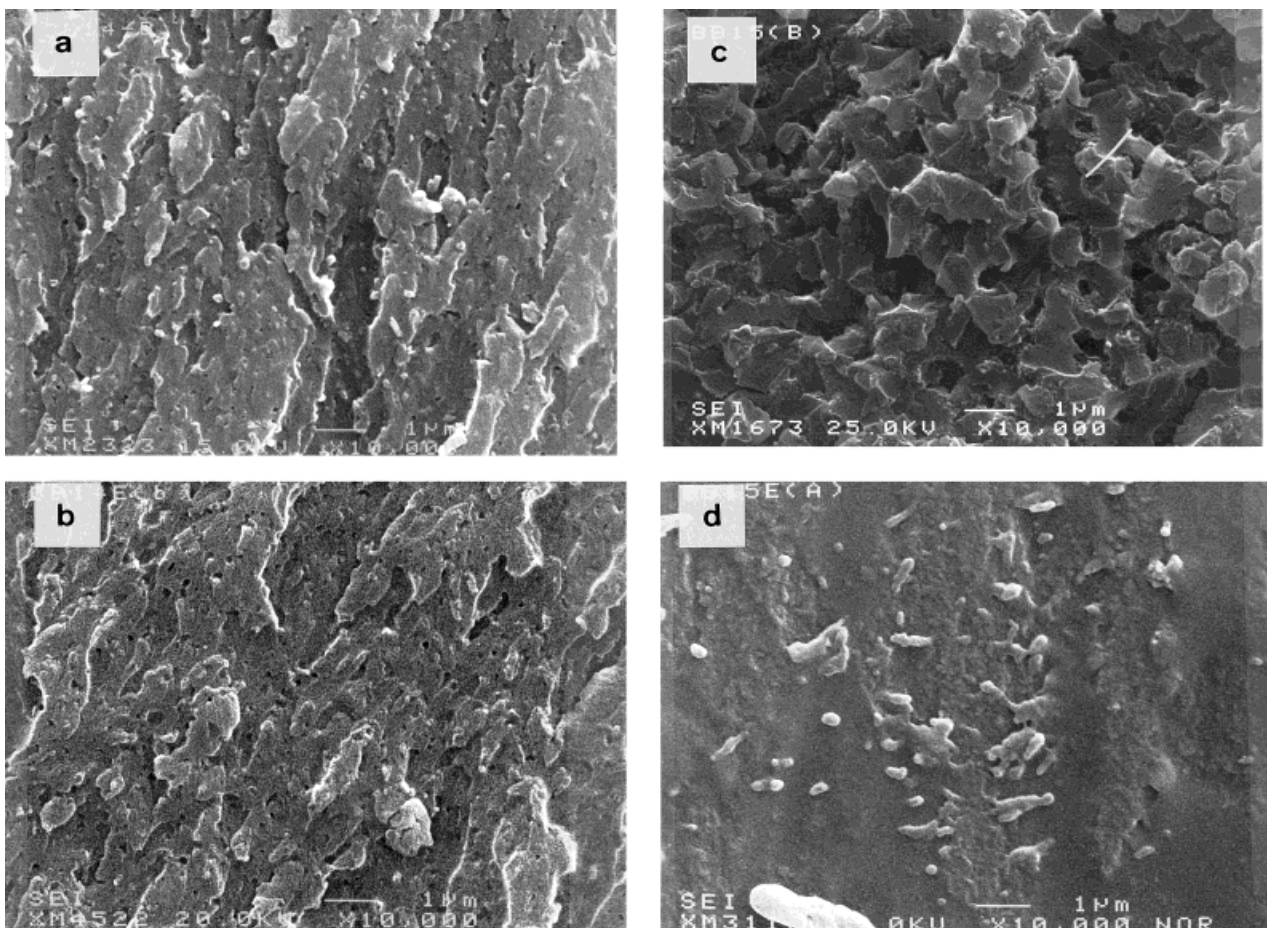


Figure 6 SEMs of fracture surfaces of PEPB-modified resins: (a) addition of 10% wt PEPB (MW = 8400); (b) addition of 10% wt PEPB (MW = 8400) after etching; (c) addition of 20% wt PEPB (MW = 8400); (d) addition of 20% wt PEPB (MW = 8400) after etching; (e) addition of 15% wt PEPB (MW = 12,300) after etching; (f) addition of 20% wt PEPB (MW = 12,300) after etching; and (g) addition of 10% wt PEPB (MW = 23,400) after etching.

crease in the magnitude of the $\tan \delta$ curve in the region from the α' -relaxation to the α -relaxation temperature. The α' -relaxation temperatures in the $\tan \delta$ curve for the PEPN-modified resins appeared as a shoulder or a small peak at about 75°C, as compared with those for the PEPT-modified materials. The peak position of the α -relaxation in the $\tan \delta$ curve for the modified resins shifted toward higher temperature with increasing molecular weight of the PEPN.

The characteristics of dynamic viscoelastic behavior of the present modified resin are the broadness of the α -relaxation peak, the increase in the magnitude of the $\tan \delta$ curve in the region above the α' -relaxation temperature, and the drop in storage modulus at room temperature. The dynamic viscoelastic behaviors are similar to those

of the PEP-modified¹⁸ and PBP-modified Matrimid resins.¹⁹

Transesterification of the Matrix and the Modifier

Dynamic viscoelastic analysis of the modified resins indicates the complexity of the matrix structure in terms of broadness of the α -relaxation peak. The exchange reaction of the polyesters and the phenolic compounds was examined in the previous study on the modification of the bismaleimide resin with PEP, PPP, PBP, and related copolyesters.^{18,19} In this study the reactions of the polyesters and DBA were carried out at a weight ratio of 20 wt% polyester inclusion by successive increases in the curing temperature according to the curing conditions. The results of transesteri-

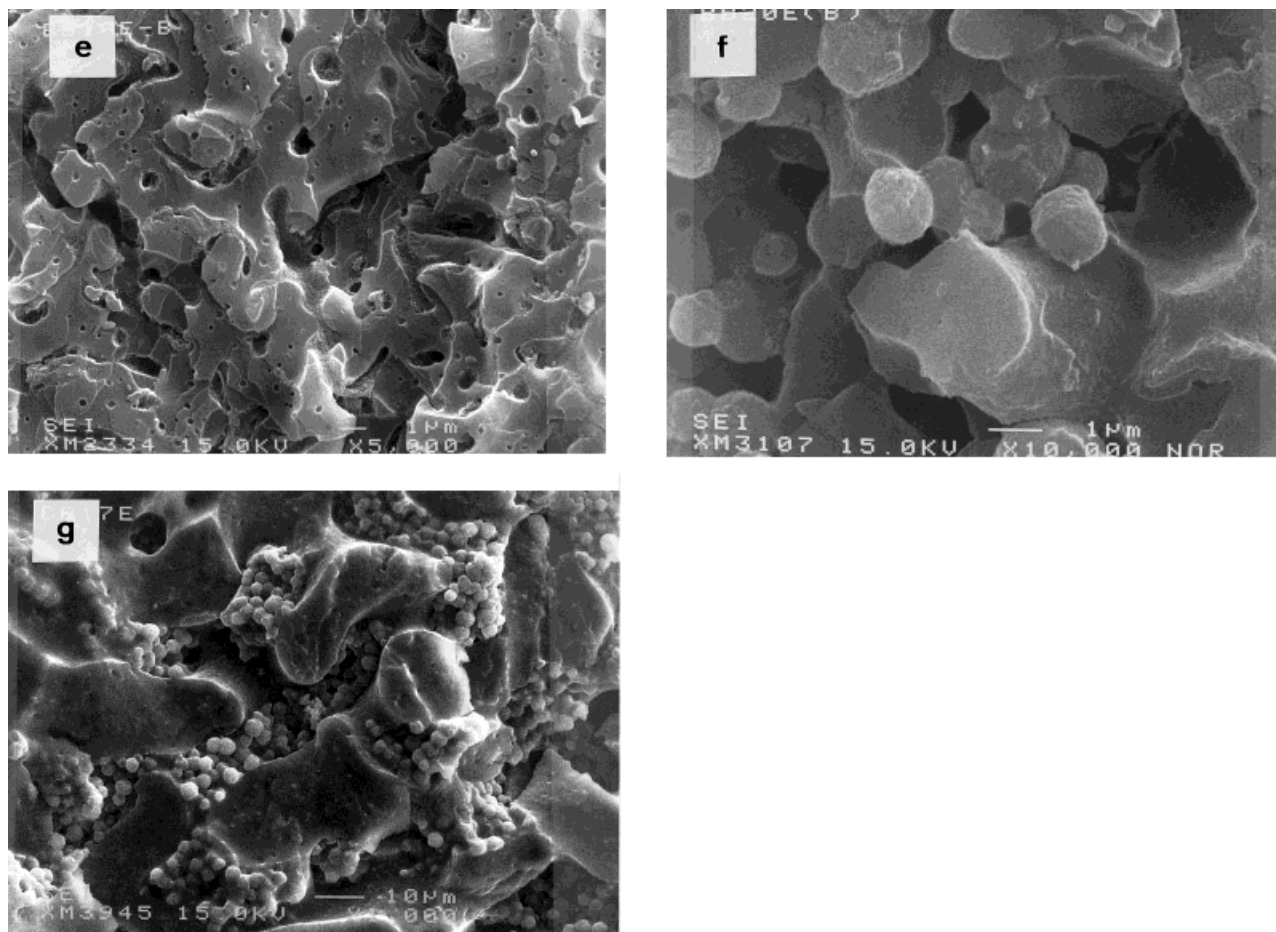


Figure 6 (Continued)

fication are collected in Table III. In the curing step up to 180°C, the molecular weight of the polyesters decreased, but transesterification could not be observed in every case. A further decrease in molecular weight and slight transesterification were observed at 200°C. The final reaction mixture after reacting at 250°C for 6 h contained some CHCl_3 -insoluble fractions because of crosslinking of the DBA: when heating the DBA alone at 250°C for 3 h, the DBA was soluble in CHCl_3 , but part of the DBA became insoluble in 6 h at 250°C, as reported previously.¹⁸ Then the extent of esterification was obtained from the resulting polymers after reacting up to for 3 h at 250°C, which was analyzed by $^1\text{H-NMR}$ spectroscopy. The molecular weight of the resulting polymer was considerably smaller than that of the beginning polyester.

The $^1\text{H-NMR}$ spectra of PEPT, PEPB, PEPN, and their resulting polymers are shown in Figures 12, 13, and 14, respectively. In the $^1\text{H-spectrum}$

of the resulting polymer after reacting PEPT (50 mol % TP unit, MW = 16,100) and DBA at 200°C for 3 h, the proton signals based on DBA could hardly be observed, and little transesterification occurred above the temperature range that end at 200°C (Table III). In the reaction at 250°C (the final stage of curing), transesterification was significant [Fig. 12(b)]: in the $^1\text{H-spectrum}$ of the resulting polymer the proton signals can be observed based on methyl, allyl, and aryl groups of DBA; 1.48 ppm for methyl groups; 3.29, 5.00, and 5.90 ppm for allyl groups; and 6.4–7.1 ppm for aryl groups, in which the molar ratio of the carboxylate and DBA units was 1:0.32 from the integrated values of the aromatic protons. The molar ratio of the PA and TP units was 0.39:0.61.

The $^1\text{H-spectrum}$ of the resulting polymer in the PEPB (50 mol % BD unit, MW = 13,800)/DBA system indicates that transesterification was low at 200°C and significant at 250°C [Fig. 13(b)]. The molar ratio of the PA and BD units was 0.40:0.60.

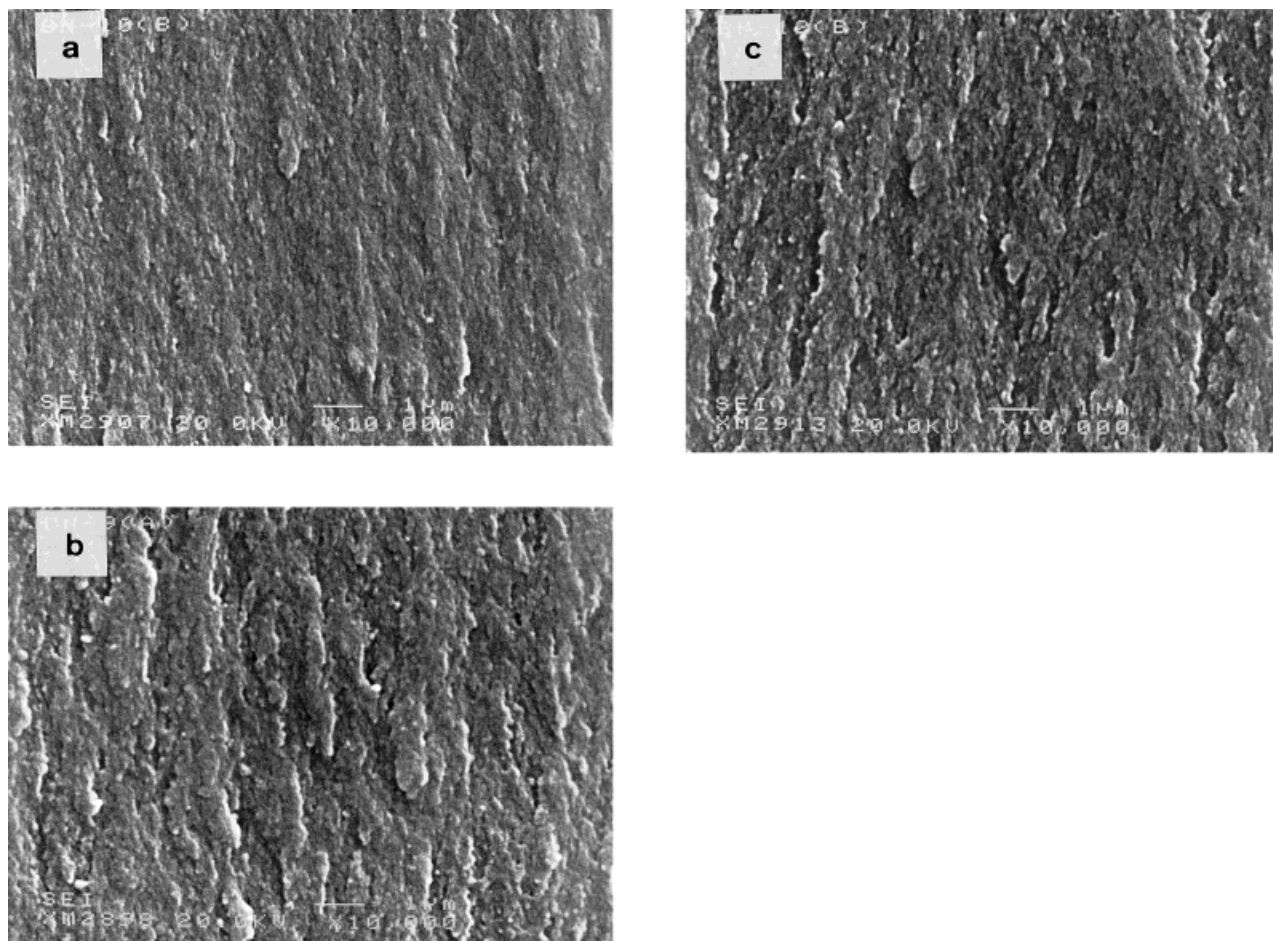


Figure 7 SEMs of fracture surfaces for PEPN-modified resins: (a) addition of 15% wt PEPN (MW = 16,100); (b) addition of 20% wt PEPN (MW = 16,100); (c) addition of 20% wt PEPN (MW = 29,400); (d) addition of 15% wt PEPN (MW = 16,100) after etching; (e) addition of 20% wt PEPN (MW = 16,100) after etching; and (f) addition of 20% wt PEPN (MW = 29,400) after etching.

Transesterification in the PEPN (50 mol % ND unit, MW = 22,300)/DBA was also low at 200°C and significant at 250°C [Fig. 14(b)]. The molar ratio of the PA and ND units was 0.40:0.60. These results indicate that the reactivity of the PA units is higher than those of the other units containing rigid groups and that parts of the resulting polymer contain the DBA-inserted structure (Scheme 2). The extent of esterification was comparable, independent of the polyester structure in the present modification systems.

To avoid the cross linking, the exchange reactions of the DBA and the aromatic polyesters were carried out in the absence of BMI. Transesterification would be retarded in the curing process by steric constraints based on a three-dimensional crosslinked structure, but a small amount

of the polyesters and DBA in the neighborhood would react with each other at the final stage (250°C) of the curing. Changes in the matrix compositions from transesterification are also shown in the viscoelastic behavior of the modified resins (Figs. 8–11).

Toughening Mechanism

All the aromatic polyesters used were soluble in bismaleimide resin without solvents and effective as modifiers for the bismaleimide resin. When using 15 wt % PEPT with a MW of 9300, the K_{IC} for the modified resin increased 75% with retention in flexural properties and a slight loss of T_g , as compared to those of the unmodified cured bismaleimide resin. The efficiency of PEPB and

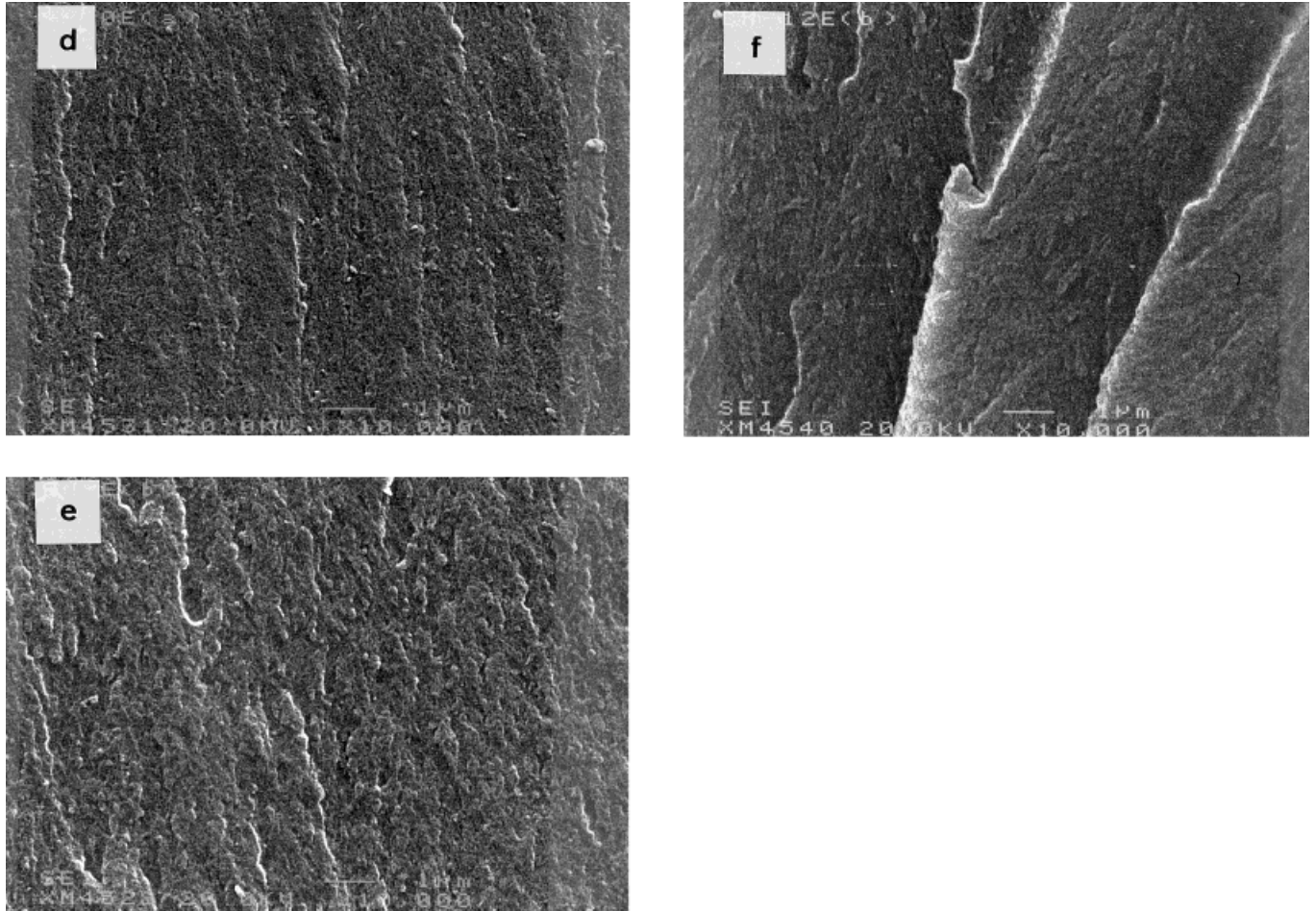


Figure 7 (Continued)

PEPN as modifiers was similar to that of PEPT. These polyesters are superior to PEP and related copolyesters because they have no deterioration of T_g . Furthermore, PEPT, PEPB, and PEPN are white solid and superior to PEP and related copolyesters (viscous liquid) in processibility.

PEP and related copolyesters are effective modifiers for a highly crosslinked epoxy matrix ($T_g = 180^\circ\text{C}$) composed of bisphenol A diglycidyl ether (DGEBA) and 4,4'-diaminodiphenyl sulfone (DDS), and its toughening mechanism has been discussed in detail.¹² In the modification with PEP, PBP, and related copolyesters, the toughening of epoxies could be attained because of the particulate structures of the modified resins. Three factors act mainly to improve the brittleness of epoxies: (1) the reinforcement of the matrix itself by incorporating the modifier, (2) the high extent of dispersion of the modifier-rich particles, and (3) the existence of relaxation near room temperature.^{12,17}

Resins modified by PEP, PPP, PBP, and related copolyesters also have particulate structures independent of polyester structure, molecular weight, and concentration. Toughening can be achieved also because of this particulate structure.^{21,22} The toughening mechanism in the bismaleimide modification with PEP and related copolyesters is similar to that in the epoxy modification with aromatic polyesters such as PEP and PBP.

Dynamic viscoelastic analysis of the present study's modification systems, which used polyesters containing higher molar ratios (50 eq. ratio) of rigid groups in the main chain, indicates that the polyesters would dissolve into the matrix to a considerable extent, as shown by broadening of the α -relaxation peak of the modified resin and by the existence of relaxation in the region from the α' -relaxation to the α -relaxation in the $\tan \delta$ curve (Figs. 8–11). It is thought that improvement of toughness in the present modification

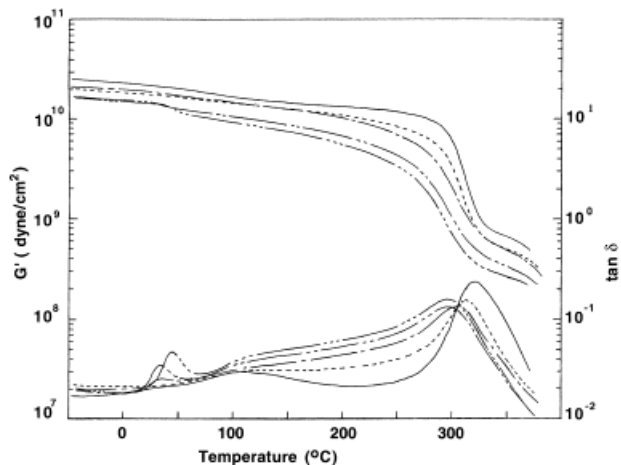


Figure 8 Dynamic viscoelastic analysis of unmodified and PEPT-modified resins (MW = 9300). PEPT inclusion (wt %): (—) 0 (control); (---) 5; (-·-) 10; (- - -) 15; and (— · —) 20.

was achievable because of the reinforcement of the matrix itself by the incorporation of the polyester as well as in the PEP and related polyester modification.

The morphologies of the modified bismaleimide resins in the present modification were slightly different from those in the PEP and related (co)polyesters modification systems. No cocontinuous or phase-inverted structures for the modified resins could be observed in previous modifications of thermosets, including epoxy,^{12,17} bismaleimide,^{18,19} and cyanate ester resins,²⁰ with the PEP

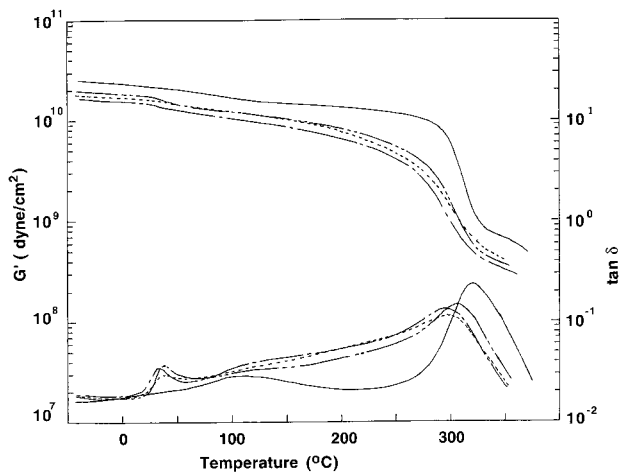


Figure 9 Dynamic viscoelastic analysis of unmodified and PEPT-modified resins (15 wt %). MW of PEPT: (—) control; (---) 6100; (-·-) 9300; and (- - -) 11,700.

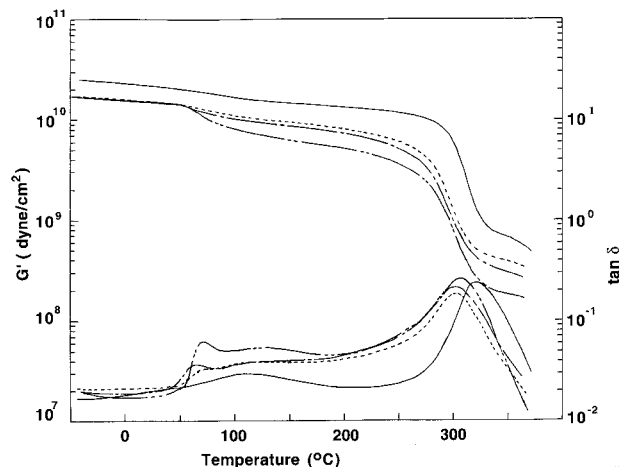


Figure 10 Dynamic viscoelastic analysis of unmodified and PEPB-modified resins (MW = 12300). PEPB inclusion (wt %): (—) 0 (control); (---) 10; (-·-) 15; and (— · —) 20.

and related (co)polyesters. When using 20 wt % PEPT (MW = 9300), the modified resin had a particulate structure [Fig. 5(c)], and the K_{IC} increased 75% (Table II, No. BT14), while the use of 20 wt % PEPT (MW = 23,700) led to macrophase separation, and the modified resin had a phase-inverted structure [Fig. 5(d)]. The phase-inverted structure was unsuitable for improvement in toughness, and the K_{IC} value for the modified resin decreased remarkably (Table II, No. BT15). Toughening could be achieved because of the particulate structure in the PEPT modification system.

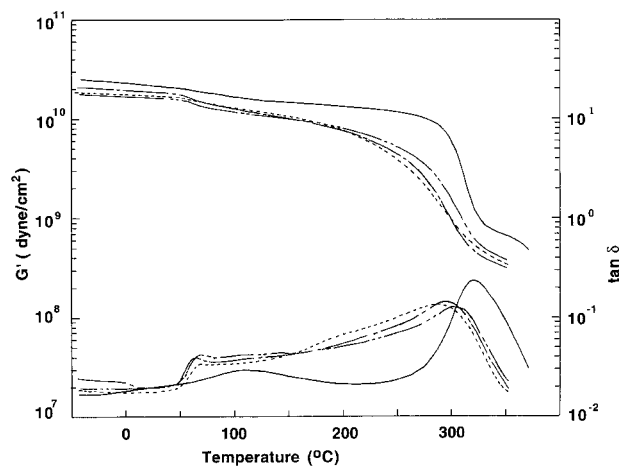


Figure 11 Dynamic viscoelastic analysis of unmodified and PEPN-modified resins (15 wt %). MW of PEPN: (—) control; (---) 6100; (-·-) 16,100; and (- - -) 29,400.

Table III Characterization of the Polymers Obtained by Transesterification

Reaction Conditions	Resulting Polymers			
	$M_{\text{GPC}}^{\text{a}}$	M_n^{a}	M_w/M_n	Carboxylate : DBA ^b
<i>PEPT-DBA series</i>				(PA : TP)
PEPT (starting polymer)	16,100	9,400	1.8	(0.47 : 0.53)
165°C/5 h	10,400	8,600	1.4	
165°C/5 h + 180°C/1 h	9,700	8,100	1.4	
165°C/5 h + 180°C/1 h + 200°C/5 h	6,900	5,100	1.5	(0.47 : 0.53) : 0.01
165°C/5 h + 180°C/1 h + 200°C/5 h + 250°C/3 h	3,100	4,300	2.1	(0.39 : 0.61) : 0.32
165°C/5 h + 180°C/1 h + 200°C/5 h + 250°C/6 h	1,800	—	—	
<i>PEPB-DBA series</i>				(PA : BD)
PEPB (starting polymer)	13,800	8,100	1.8	(0.52 : 0.48)
165°C/5 h	10,400	8,400	1.4	
165°C/5 h + 180°C/1 h	9,100	7,800	1.4	
165°C/5 h + 180°C/1 h + 200°C/5 h	3,900	3,500	1.4	(0.47 : 0.53) : 0.06
165°C/5 h + 180°C/1 h + 200°C/5 h + 250°C/3 h	3,100	4,000	2.3	(0.40 : 0.60) : 0.45
165°C/5 h + 180°C/1 h + 200°C/5 h + 250°C/6 h	3,500	—	—	
<i>PEPN-DBA series</i>				(PA : ND)
PEPN (starting polymer)	22,300	12,700	1.8	(0.48 : 0.52)
165°C/5 h	16,400	12,600	1.5	
165°C/5 h + 180°C/1 h	14,500	11,100	1.5	
165°C/5 h + 180°C/1 h + 200°C/5 h	5,100	4,200	1.4	(0.49 : 0.51) : 0.03
165°C/5 h + 180°C/1 h + 200°C/5 h + 250°C/3 h	3,100	3,900	2.2	(0.40 : 0.60) : 0.38
165°C/5 h + 180°C/1 h + 200°C/5 h + 250°C/6 h	1,800	—	—	

^a By GPC.^b By ¹H-NMR. Unit molar ratio.

In the modification with PEPB, the modified resin had a particulate structure on inclusion of 15 wt % PEPB [MW = 12,300; Fig. 6(e)] and its K_{IC} increased 75% (Table II, No. BB18), while the morphology of the modified bismaleimide resin became a phase-inverted structure on inclusion of 20 wt % of the same modifier [Fig. 6(f)], and the K_{IC} for the modified resin decreased (Table II, No. BB20). The modified resin had a cocontinuous phase structure on inclusion of 10 wt % high MW (23,400) PEPB [Fig. 6(g)]; the K_{IC} value increased 75% (Table II, No. BB17). Particulate or cocontinuous phase structures were suitable for improving the brittleness of the cured resin in the PEPB modification system.

The PEPN-modified resins were transparent. The modified resin had a particulate structure (less than 0.1 μm in diameter) independent of PEPN MW and concentration. When using 20 wt % PEPN (MW = 16,100), the K_{IC} value increased 65% (Table II, No. BN19). Toughening could be achieved because of the particulate structure in the PEPN modification system.

The morphological behavior of the modified resin can be explained to some extent in terms of

solubility parameter (δ). The δ values [(MJ/m³)^{1/2}] for the Matrimid A/B resin, PEPT, PEPB, PEPN, and PEP are 27.30, 23.53, 23.30, 23.66, and 25.40, respectively (by Fedors's method).²¹ The δ values indicate that miscibility of the aromatic polyesters used with the bismaleimide matrix in this study is lower than that of PEP. The morphological behaviors in the PEPT and PEPB modification could be a result of lower miscibility of the polyesters with the bismaleimide resin, while the PEPN-modified resin had a particulate structure independent of PEPN MW and concentration, although the δ value of PEPN was similar to those of PEPT and PEPB. Furthermore, transesterification in the final stage of curing would promote miscibility of the polyesters, yet the results indicate that the extent of transesterification was independent of the present polyester structure (Table III). Hence, morphological behavior in the PEPN modification cannot be explained in terms of solubility parameter and transesterification. At present it remains to be elucidated why the miscibility of PEPN with the bismaleimide resin was higher than those of the others.

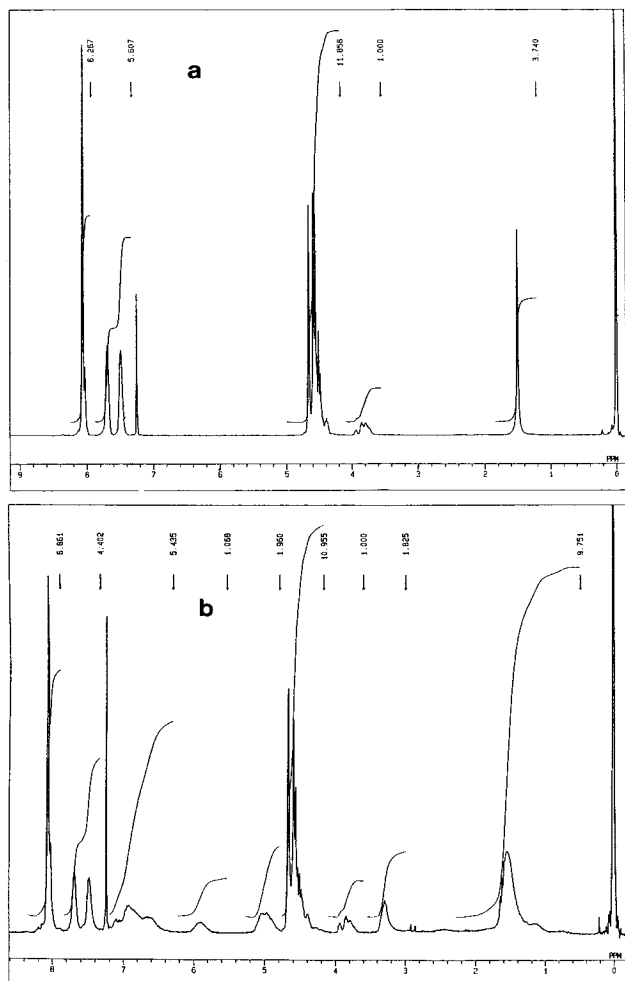


Figure 12 $^1\text{H-NMR}$ spectra of the polymer resulting from the reaction of PEPT and DBA with solvent CDCl_3 at 60°C : (a) PEPT, and (b) after 3 h at 250°C .

The existence of relaxation near room temperature is also important for improving the brittleness of the thermosets because the presence of the relaxation peak enhances the toughness of epoxies, as a result of the increase in the plastic zone from the rise in temperature at the crack front.^{22,23} Recently, we reported that the existence of relaxation near room temperature is important for improving the brittleness of epoxy, bismaleimide, and cyanate ester resins in the modification with PEP and related polyesters.^{12,17–20} In the present modification the existence of α' -relaxation peaks in the $\tan \delta$ curves were also observed.

In the present modification the above three factors acted to improve the toughness of the bismaleimide resin, but these factors could not be evaluated separately. So it is difficult to de-

scribe what is the main toughening mechanism. However, the morphology of the modified resin may be the more important factor in modification of the bismaleimide resin, given that the phase-inverted structure is unsuitable for improvement in toughness, although the reinforcement of the resin itself by aromatic polyesters is generally important for improving toughness in the modification of the thermosets by aromatic polyesters.

CONCLUSIONS

The aromatic polyesters containing rigid groups in the main chain (PEPT, PEPB and PEPN) were shown to be effective modifiers for the Matrimid resin. For example, inclusion of 20 wt % PEPT



Figure 13 $^1\text{H-NMR}$ spectra of the polymer resulting from the reaction of PEPB and DBA with solvent CDCl_3 at 60°C : (a) PEPB, and (b) after 3 h at 250°C .

(MW = 9,300) led to a 75% increase in K_{IC} with retention in flexural properties and a slight loss of T_g , as compared with those of the unmodified cured bismaleimide resin. The efficiency as modifiers of PEPB and PEPN was similar to that of PEPT. In the PEPT and PEPN modification systems the particulate structures of the modified resins were suitable morphologies for improving the brittleness of the cured resins. Hence, the toughening mechanism in these modification systems is similar to that in the thermosets modified with PEP and (co)related polyesters. In the PEPB modification system toughening could be achieved because of particulate or cocontinuous phase structures. These polyesters are superior to PEP and related (co)polyesters both in retention of T_g and in processibility.

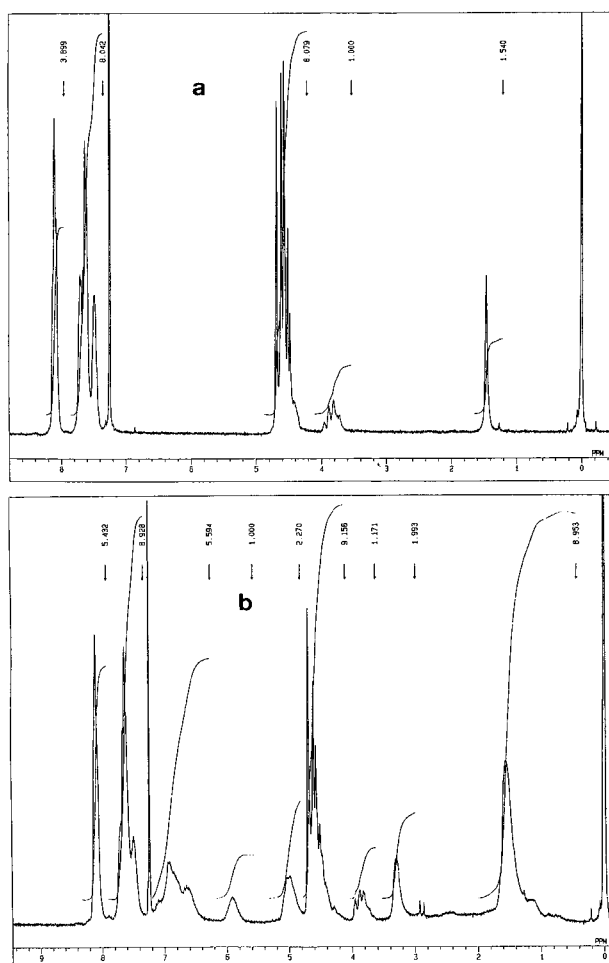
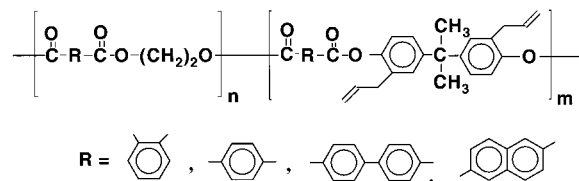


Figure 14 $^1\text{H-NMR}$ spectra of the polymer resulting from the reaction of PEPN and DBA with solvent CDCl_3 at 60°C : (a) PEPN, and (b) after 3 h at 250°C .



Scheme 2 Structure of aromatic polyesters after transesterification.

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