Toughening of Bismaleimide Resin by Modification with Poly(ethylene phthalate) and Poly(ethylene phthalate-*co*-ethylene isophthalate)

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ABSTRACT: Aromatic polyesters were prepared and used to improve the brittleness of the bismaleimide resin composed of 4,4′-bismaleimidediphenyl methane and *o,o′*-diallyl bisphenol A. The aromatic polyesters contain poly(ethylene phthalate)(PEP) and poly(ethylene phthalate-*co*-ethylene isophthalate) (10 mol % isophthalate unit) (PEPI). PEP and PEPI were effective modifiers for improving the brittleness of the bismaleimide resin. The most suitable composition for the modification of the bismaleimide was inclusion of 20 wt % PEP (MW 18,200), which led to an 80% increase in the fracture toughness with retention of flexural properties and a slight decrease in the glass transition temperature, compared with the mechanical and thermal properties of the unmodified cured bismaleimide resin (Matrimid resin). Microstructures of the modified resins were examined by scanning electron microscopy and dynamic viscoelastic analysis. The thermal stability of the modified resin was slightly lower than that of the unmodified resin by thermogravimetric analysis. The toughening mechanism is discussed in terms of the morphological and dynamic viscoelastic behavior of the modified bismaleimide resin system. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **65:** 1349–1357, 1997

Key words: bismaleimide resin; modification; poly(ethylene phthalate); poly(ethylene phthalate-*co*-ethylene isophthalate); fracture toughness

INTRODUCTION

Addition polyimide resins are among the most important thermosetting polymers and have received attention because of high thermal stability and mechanical properties. The drawback of the polyimide resins is that they are brittle and difficult to process. Bismaleimide resins were also investigated because of good processability and nonvolatility. Recently a two-component bismaleimide system (Matrimid 5292 A and B), composed of 4,4′-bismaleimidediphenyl methane (BMI) and *o,o′*-diallyl bisphenol A (DBA), has been devel-

oped by Ciba Geigy Corp. (Switzerland) to improve mechanical properties and processability.[1] DBA copolymerizes with BMI via an ene reaction during curing. The brittleness of the cured resin was improved, compared with the conventional bismaleimide resins, but its 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] or engineering thermoplastics (e.g., polysulfones (PSF)[3–5] or poly(ether imide) (PEI)[6–8]). Engineering thermoplastics are interesting materials as modifiers for bismaleimide resins from the viewpoint of the maintenance of mechanical and thermal properties for

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Table I   Characterization of Aromatic Polyesters

Entry Number	Polyester Composition (mol %)	M_{GPC}[a] (10^3)	M_n[a] (10^3)	M_w/M_n	T_g[b] (°C)
PEP					
3	—	7.7	5.6	1.6	—
2	—	9.6	6.7	1.6	26
4	—	12.6	8.4	1.7	—
1	—	18.2	11.7	1.7	27
5	—	26.7	16.3	1.8	30
PEP I					
3	IP 10	4.9	3.5	1.7	—
2	10	7.7	4.9	1.8	—
4	10	10.3	6.3	1.8	—
1	10	14.1	8.1	1.9	30

[a] By GPC.
[b] By DSC.

the matrix resins. PSF, PEI, and polyhydantoin were used as modifiers in the modification of the Compimide 796/Compimide TM 123 [4,4′-bis(o-propenylphenoxy)benzophenone] system (Technochemie Co., Germany).[9] The Compimide/PEI modification systems were examined in detail.[10] Engineering thermoplastics such as PEI, poly-(ether sulfone), and poly(ether ketone ketone) were used for the BMI/diallyl compounds systems, where the diallyl compounds included Matrimid B (DBA), Compimide TM 121 [bis(allylphenyl)ether], and Compimide TM 123.[11] Three structurally different poly(ether ketone)s (PEKs) were used in the modification of the Compimide 796/Compimide TM 123 system to examine the effects of PEK structure, molecular weight, and concentration on the fracture behavior.[12] Furthermore, functionalized PEKs having pendant propenyl groups were prepared and used as tougheners for the Compimide 796/Compimide TM 123 system.[13] Amorphous functionalized engineering plastics such as PSF, 6F polyimide, and poly(arylene ether phosphine oxide) were prepared and used as modifiers for toughening the Matrimid 5292 A/B system.[14]

Modification of the bismaleimide resin (the Matrimid 5292 system) has been carried out on the basis of information on the toughening of epoxies by thermoplastics in our laboratory.[15–23] For example, N-phenylmaleimide–styrene copolymers were effective modifiers for both epoxy[18,19] and bismaleimide resins.[24,25] In previous papers we have reported that poly(ethylene phthalate) (PEP) and the related copolyesters were effective modifiers for the epoxy resins.[15,21]

This paper reports the modification of the bismaleimide resin (the Matrimid 5292 A/B system) by aromatic polyesters. PEP and poly(ethylene phthalate-co-ethylene isophthalate) [10 mol % isophthalate (IP) unit] (PEPI) were used as modifiers for the bismaleimide resin, considering the modification results of highly crosslinked epoxy matrices by the aromatic polyesters.[21] The effects of structure, molecular weight (MW), and amount of the polyesters used on the toughness of the cured resins were examined.

EXPERIMENTAL

Materials

The bismaleimide resin was a commercial product composed of BMI and DBA (Ciba Geigy Corp., Matrimid 5292 A/B). PEP and PEPI were prepared by the reaction of 1,2-ethanediol and aromatic dicarboxylic acids (phthalic anhydride and isophthalic acid) reported previously.[15] Other reagents were used as received.

Measurements

^{1}H-NMR spectra were recorded on a 90 MHz instrument (JEOL JNM-9MX 90) at 60°C using CDCl$_3$ as solvent and tetramethylsilane as internal standard. The molecular weight of the polyester was measured by gel permeation chromatography (GPC) (Shimadzu LC-5A instrument) using polystyrene standards. The mechanical properties of the cured resins were determined with a Shi-
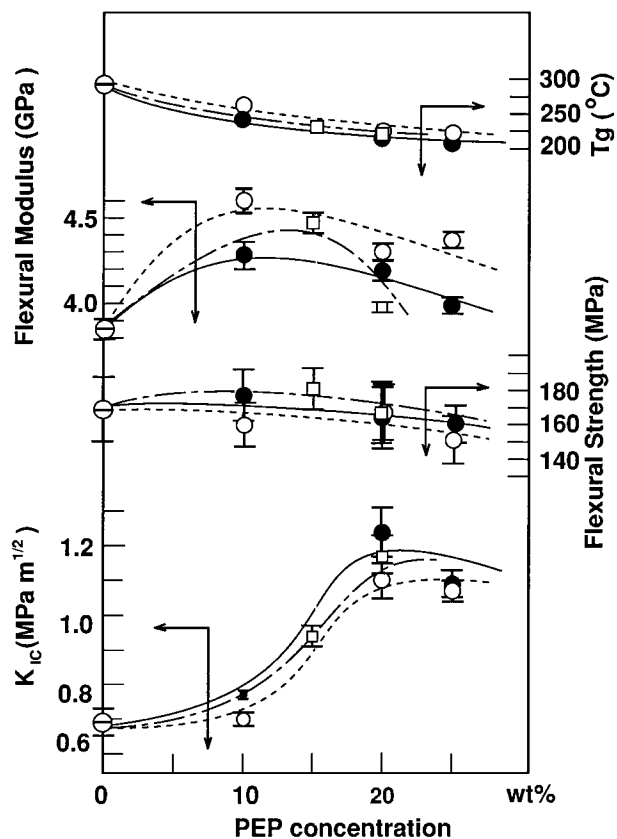
Figure 1 Physical properties of the modified resins as functions of PEP concentration. ($\ominus$) control; ($\bigcirc$) MW (12,600); ($\bullet$) MW (18,200); ($\square$) MW (26,700).

madzu autograph AGS-500B universal testing machine. Flexural tests were carried out at a crosshead speed of 2 mm/min (JIS K7203). The fracture toughness, K_{IC}, was measured in a three-point bent geometry at a crosshead speed of 1 mm/min (ASTM E-399). The dimensions of the K_{IC} specimens are approximately $7 \times 14 \times 82$ mm. A central notch (ca. 5.5 mm in length) was machined with a diamond wheel saw, while cooling with water, and the specimen was dried. A sharp starter crack (ca. 1.5 mm in length) was introduced at the base of the notch by a new razor blade. The specimen numbers used were at least five. The glass transition temperatures (T_gs) of the polyesters were measured as the onset temperatures by differential scanning calorimetry (Shimadzu DSC 41M type) at a heating speed of 10°C/min. The T_gs of the cured resins were obtained by thermal mechanical analysis (Shimadzu TMA 40M type, the penetration mode) at a heating speed of 5°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 −50 and 400°C at a heating speed of 5°C/min at frequency of 1 Hz. Thermogravimetric analysis (TGA) was carried out at a heating rate of 10°C/min under nitrogen using a Shimadzu TGA 40.

Curing Procedure

The polyesters were dissolved into DBA at 130°C without solvents. Then BMI was added to the mixture, which was kept at 130°C to dissolve the BMI. The resulting clean mixture was degassed *in vacuo* at 130°C. BMI and DBA were used in an equivalent ratio of 1 : 1. The mixture was poured into molds, preheated to 130°C, to obtain 4- or 7-mm-thick plaques. The mold consisted of one pair of upright and metal clip-held glass plates spaced by U-shaped silicon rubber stick. The amount (wt %) of the modifier was calculated based on the matrix resin. The curing cycle was 160°C for 3 h + 180°C for 1 h + 200°C for 2 h + 250°C for 6 h.
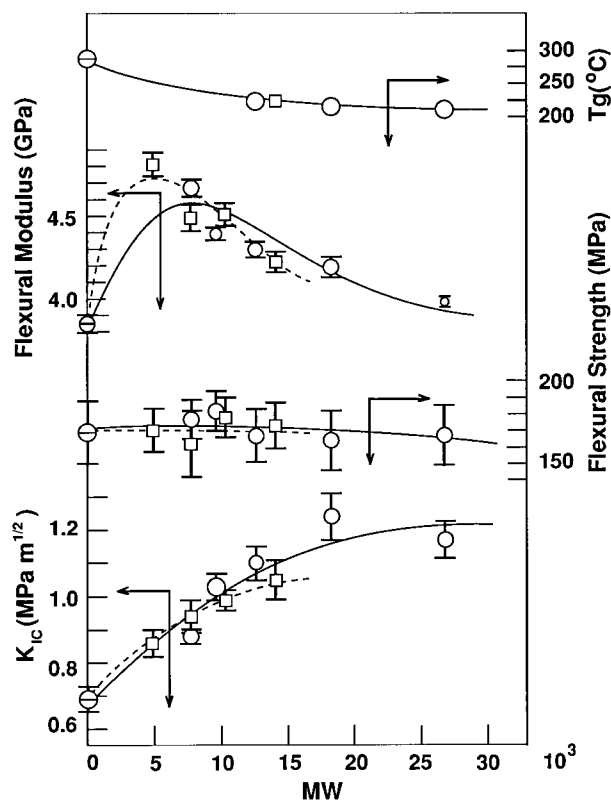

Figure 2 Dependence of physical properties of the modified resins on polyester MW on 20 wt % addition. ($\ominus$) control; ($\bigcirc$) PEP; ($\square$) PEPI (10 mol % IP unit).
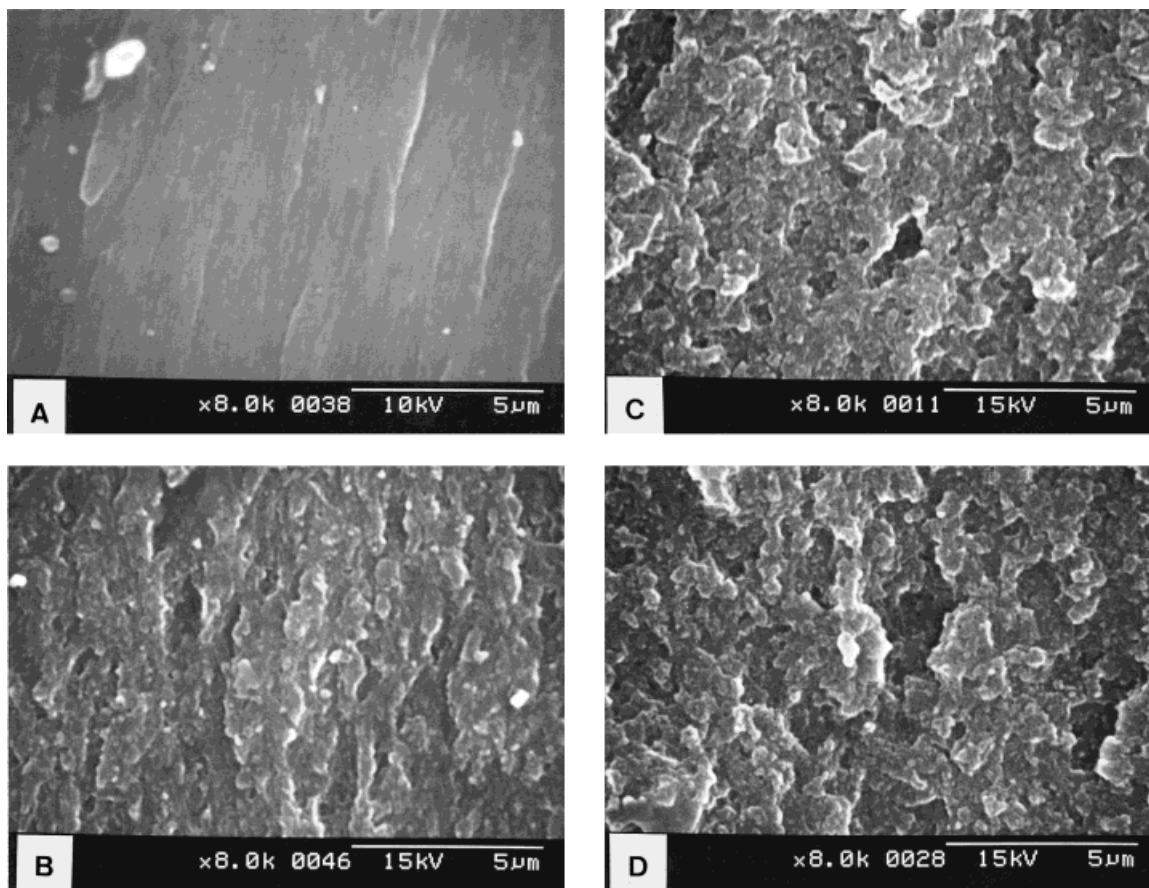
Figure 3 SEM of fracture surfaces for the modified resins. (A) PEP (MW 18,200) 10 wt % addition; (B) PEP (MW 18,200) 20 wt % addition; (C) PEP (MW 18,200) 25 wt % addition; (D) PEP (MW 26,700) 20 wt % addition.

After curing, the oven temperature was decreased from 250°C to 50°C at a cooling rate of 25°C/h.

Reaction of PEP with Phenols

Transesterification of PEP and DBA or bisphenol A during curing was examined as follows. PEP was dissolved into DBA in the weight ratio of 20 wt % PEP inclusion and the reaction was carried out under the same reaction conditions as with the curing. After the reaction was over, the reaction mixtures were diluted with $CHCl_3$ and a polymer was isolated using methanol as precipitant. The polymer was purified twice by reprecipitation with $CHCl_3$/methanol and dried *in vacuo* at 80°C. The recovery of the polymer was 78%. The resulting polymer was analyzed by ^{1}H-NMR spectroscopy (60°C in $CDCl_3$) and GPC. The polymer was recovered 77% in the reaction at lower temperature up to 200°C for 2 h. PEP and bisphenol A (mp 156–159°C) were homogenized

at 160°C and heated under the curing conditions. The reaction product was obtained in 24% yield.

RESULTS AND DISCUSSION

Characterization of Aromatic Polyesters

In this study various molecular weights of PEP and PEPI were prepared in quantitative yield by polycondensation of 1,2-ethanediol and aromatic dicarboxylic acids (phthalic anhydride and iso-phthalic acid) as reported previously.[15] Table I reports some characteristic properties of the aromatic polyesters. The GPC-average molecular weight (M_{GPC}), obtained from the peak position of GPC curve, was used as a measure of the MW in this article as well as in the previous article[15,21] because the number-average molecular weight is highly sensitive to the presence of a small amount of lower-molecular-weight materials.
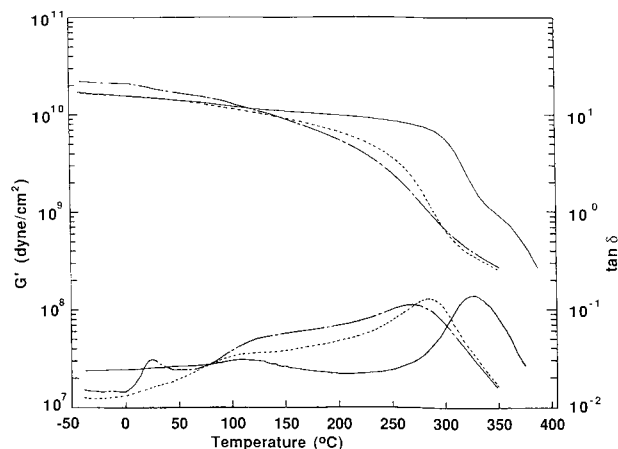
Figure 4 Dynamic viscoelastic analysis for unmodified and PEP-modified resins. (——) 0 wt % (control); (------) PEP (MW 18,200) 10 wt %; (— – —) PEP (MW 18,200) 20 wt % addition.

Mechanical and Thermal Properties of Modified Bismaleimide Resins

The unmodified bismaleimide resin was transparent. The modified resins became translucent during curing. Figure 1 shows the mechanical and thermal properties of the modified resins as a function of PEP concentration. The K_{IC} for the modified resins increased with increasing PEP concentration up to 20 wt % addition of the modifier and leveled off, independent of PEP MW. Flexural strength for the modified resins was equal to or larger than that for the unmodified resin. It is noteworthy that flexural moduli for the modified resins were significantly higher than for the unmodified resin. The T_g values decreased gradually with increasing PEP concentration.

Figure 2 shows the dependence of physical properties of the modified resin on the modifier MW on 20 wt % inclusion. The K_{IC} for the modified resins increased with increasing PEP MW and leveled off. Flexural strength for the modified resins was comparable with that for the unmodified resin. Flexural moduli for the modified resins were significantly larger than that for the unmodified resin. This indicates that the matrix compositions would change because of incorporated polyester as shown in dynamic viscoelastic behavior. PEP having MW more than 18,200 were most effective modifiers and the use of 20 wt % of the PEP (MW 18,200) led to an 80% increase in K_{IC} with no loss of flexural properties. PEPI (10 mol % IP unit) were slightly less effective as modifiers for the bismaleimide resin than PEP.

Microstructures of the Modified Bismaleimide Resins

The morphologies of the cured resins were investigated by the SEM. The unmodified cured Matrimid resins had only one phase, as reported previously.[24] Figure 3 shows SEM for the PEP-modified resins etched by chloroform (3 days). The fracture surface of the PEP (MW 18,200) 10 wt %-modified resin was relatively smooth and featureless [Fig. 3(A)]. When using 20 wt % of the same modifier, the fracture surface became rough and fine particles less than 1 μm were observed, but the contours of the particles were vague, perhaps because of transesterification of DBA and PEP as shown later [Fig. 3(B)]. The fracture surface became rougher on 25 wt % inclusion of the same modifier and the contours of the particles were also obscure [Fig. 3(C)]. The fracture surfaces became rougher with increasing PEP concentration and MW, perhaps because of the increase in the plastic deformation of the crack tip in the process of the crack propagation [Fig. 3(C,D)]. The SEM of the PEPI-modified resins were similar to those of the PEP-modified resins.

Dynamic viscoelastic analysis can give information on the microstructure of cured resins. Figure 4 shows the storage moduli, G', and tan δ curves for the unmodified and PEP-modified resins. When using 10 wt % of PEP (MW 18,200), the peak position of the α-relaxation in the tan δ curve shifted considerably toward lower temperature, its shape became broader, and the magni-
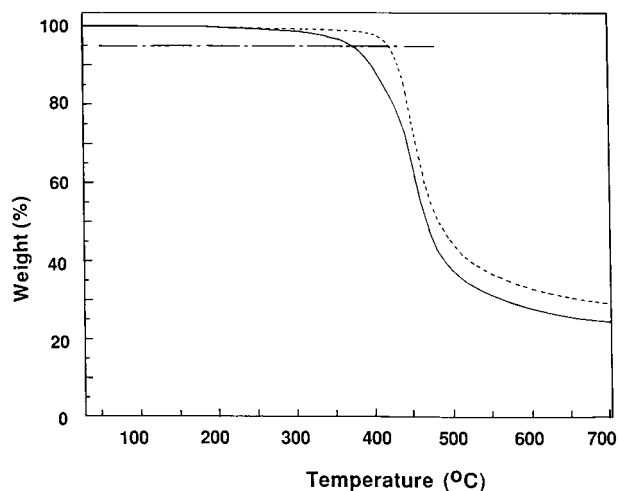

Figure 5 TGA of the unmodified and PEP-modified resins. (-----) 0 wt % (control); (——) PEP (MW 18,200) 20 wt %.

tude of the tan δ curve increased in the region from room temperature to the α-relaxation peak temperature to a considerable extent, compared with dynamic viscoelastic behavior for the cured Matrimid resin. The broadness of the α-relaxation and the increase in the magnitude of the tan δ curve above room temperature indicate the complexity of the matrix structure, which would perhaps be because of PEP incorporating into the network. In the modification of the bismaleimide resin with 20 wt % of PEP, the α-relaxation peak became even broader, its position shifted toward lower temperature, and its magnitude became lower, compared with those for the unmodified resin and the PEP (10 wt %)-modified resin. A new relaxation peak (α'-relaxation) was observed at 24.5°C on 20 wt % addition of PEP. The appearance of the new α'-relaxation peak in the tan δ curve indicates the existence of the phase-separated structure for the PEP (20 wt %)-modified resin. The storage moduli at room temperature for the modified resin were equal to or larger than those for the unmodified resin. These dynamic viscoelastic behaviors correspond to the morphologies of the modified resins.

TGA was carried out under N_2 to examine the thermal stability of the modified resin (Fig. 5). The parent cured Matrimid resin was stable at high temperature and underwent a weight loss of 5% at 422°C. A loss weight of 5% occurred at 377°C for the PEP (MW 18,200) 20 wt %-modified

Figure 6 GPC profiles. Solvent: THF; elution rate: 1 mL/min. (——) PEP; (– – – –) THF-soluble fraction of the resulting polymer from the reaction of DBA and PEP under the curing conditions; (— – —) reaction product of PEP and bisphenol A.

resin. The thermal stability of the modified resin was lower than that of the unmodified resin.

Transesterification of the Matrix and the Modifier

The dynamic viscoelastic analysis of the PEP-modified resins indicated the complexity of the matrix structure. To clarify whether the exchange reaction of ester and phenolic groups would occur, the reaction of DBA, phenolic component, and PEP (MW 26,700) was carried out in the weight ratio on 20 wt % inclusion under the curing conditions (up to 250°C for 6 h). The reaction mixture contained some chloroform-insoluble fractions which would be based on the radical reaction of allyl group in DBA or the addition reaction of allyl and phenolic groups: when heating DBA alone at 250°C for 3 h, DBA was soluble in chloroform, but part of DBA became insoluble after 6 h at 250°C. The resulting polymer was partly insoluble in tetrahydrofuran (THF). Then the THF-soluble fraction of the polymer was analyzed by GPC. Figure 6 shows GPC profiles of PEP and the THF-soluble fraction of the resulting polymer. The MW distribution of the latter polymer was significantly larger than that of PEP and MW (15,500) of the polymer decreased. Figure 7(A,B) shows ^{1}H-NMR spectra of PEP and the resulting polyester. The ^{1}H-NMR spectrum of the polyester was different from that of PEP. In the former spectrum the proton signals are observed based on methyl, allyl, and aryl groups of DBA: 1.54 ppm for methyl groups; 3.28, 4.97, and 5.89 ppm for allyl groups; and 6.4–7.1 ppm for aryl groups; where the molar ratio of phthalate and DBA units was 1 : 0.53 from the integrated values of the aromatic protons. It is difficult to determine the extent of esterification, considering the gelation of DBA alone at 250°C. Part of the polymer would contain the DBA-inserted structure (Scheme 1). When reacting DBA and PEP (MW 26,700) at lower temperature up to 200°C (2 h), transesterification hardly occurred and the molar ration of phthalate and DBA units was 1 : 0.02 [Fig. 7(C)]. Furthermore, to avoid the contamination of the polyester by homopolymerization of DBA, the model reaction was carried out using bisphenol-A in place of DBA under the same reaction conditions (up to 250°C). The polymer was soluble in THF and its MW (1,800) decreased considerably compared with PEP (MW 26,700) (Fig. 6). Figure 7(D) shows ^{1}H-NMR spectra of the reaction products. Methyl and aryl proton signals are observed at 1.54 and 6.5–7.35 ppm, respectively, and the molar ratio of phthal-
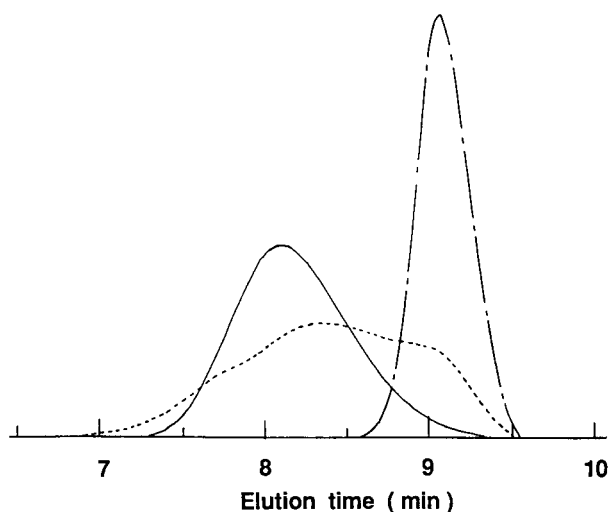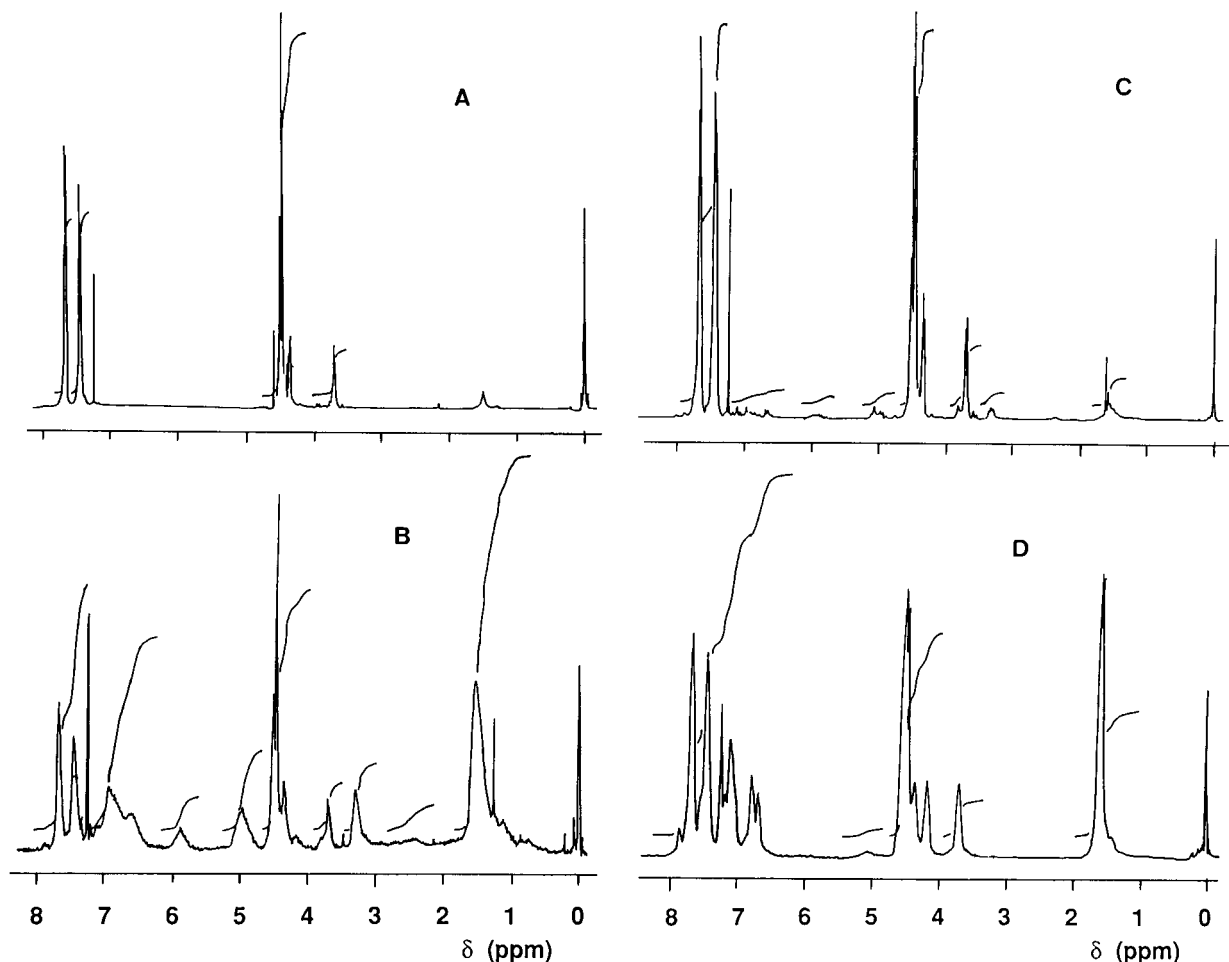
Figure 7 ^{1}H-NMR spectra. Solvent CDCl$_3$ at 60°C. (A) PEP; (B) the resulting polymer in the reaction of DBA and PEP under the curing conditions; (C) the resulting polymer in the reaction of DBA and PEP at lower temperature up to 200°C; (D) reaction product of PEP and bisphenol-A.

ate and bisphenol A units was 1 : 0.36. In this reaction system no crosslinking occurs, and the existence of methyl and aryl groups based on bisphenol A clearly indicates the insertion of a bisphenol A unit into the PEP main chain. These results indicate that esterification between PEP and phenolic groups occurs at 250°C to considerable extent, and that the exchange reactivity between PEP and DBA is lower than that between PEP and bisphenol-A because of the steric hindrance due to o-substitution.

The above exchange reactions were carried out in the absence of BMI to avoid the crosslinking. In the curing process the steric constraints based on the three-dimensional crosslinked structure will prevent esterification occurring, but some PEP and DBA located in the neighborhood would react with each other at the final stage (250°C)

of the curing beyond the T_g (210–225°C) of the modified resins. Then the matrix compositions will change by transesterification between DBA and PEP, as shown in the viscoelastic behavior of the PEP-modified resins (Fig. 4).

Toughening Mechanism

PEP and PEPI (10 mol % IP unit) were effective as the modifiers for the bismaleimide resin. PEP and PEPI (10 mol % IP unit) were soluble in the bismaleimide resin without solvents. PEP having MW 18,200 was most effective among them. The efficiency of PEPI (10 mol % IP unit) was slightly less than PEP. The most suitable composition for the modification of the bismaleimide resin was inclusion of 20 wt % of PEP (MW 18,200), which

led to 80% increase in K_{IC} with retention in flexural properties.

PEP and the related copolyesters were effective modifiers for highly crosslinked epoxy matrix (T_g 180°C) composed of bisphenol A diglycidyl ether (DGEBA) and 4,4′-diaminodiphenyl sulfone (DDS), and the toughening mechanism has been discussed in detail.[21] The toughening of epoxies could be attained by the particulate structures (PEP-rich particles less than 1 μm in diameter) of the modified resins, and three factors would 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 the relaxation near room temperature. Poly(butylene phthalate) (PBP) and the related copolyesters were also effective modifiers for the DDS-cured DGEBA resin.[26] The toughening mechanism in the PBP modification system is similar to that in the modification with PEP.

In the present modification system the morphologies of the modified bismaleimide resins were not clear by SEM, though the dynamic viscoelastic analysis indicates the existence of the phase-separated structure in some cases. The morphological behavior in the modification of the bismaleimide with PEP can be explained in terms of solubility parameter (SP). The SP value [27.66 $(MJ/m^3)^{1/2}$] of the Matrimid A/B resin is close to that (25.40) of PEP (by Fedors' method[27]), indicating high miscibility of PEP with the bismaleimide matrix. Furthermore, the reaction of DBA and PEP at 250°C indicates the occurrence of transesterification. Transesterification of DBA and PEP would also enhance miscibility of PEP with the bismaleimide matrix by chemical blending, though the extent of transesterification in the curing process is unknown because of the insoluble crosslinked structure of the PEP-modified bismaleimide resin. Dynamic viscoelastic analysis also indicates that PEP would dissolve into the matrix to considerable extent, as shown in broadening of the α-relaxation peak of the modified resin (Fig. 4). It is thought that the improvement of toughness in the present modification could be achieved because of the reinforcement of the matrix itself by the incorporation of the polyester, similar to the modification of epoxies with the aromatic polyesters.

The existence of the relaxation peak near room temperature is also important in improving the brittleness of the thermosetting polymers. Recently it was reported that the presence of the β-
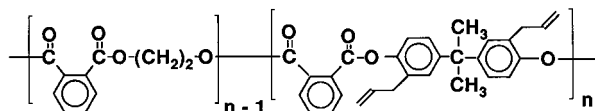
Scheme 1

relaxation peak near room temperature was effective in improving the toughness of epoxies because the increase in the plastic deformation zone contributed to the increase in temperature at the crack front.[28,29] We have also reported that several relaxations at more than 50°C contribute to toughening of epoxies in the modification of the DDS-cured DGEBA resins with butyl acrylate–glycidyl acrylate copolymers.[30] Most recently, we reported that the existence of the relaxations near room temperature is important in improving the brittleness of epoxies in the modification of the DDS-cured DGEBA resins with PEP, PBP, and the related copolyesters.[21,26] In the present modification the α'-relaxation peak was not observed on 10 wt % addition of PEP (MW 18,200), but the magnitude of the tan δ curve increased from room temperature to the α-relaxation temperature to a considerable extent, which is thought to be because of an overlapping of various small relaxations based on PEP incorporation into the bismaleimide matrix. When using 20 wt % of the same modifier, the α'-relaxation peak appeared at 24.5°C and the increase in the magnitude of the tan δ curve from 50°C to the α-relaxation temperature was more significant. These relaxations would be effective in toughening the cured bismaleimide resins.

In the modification of epoxies with PEP, the modified resins have particulate morphologies with well-dispersed PEP-rich particles in the matrix. In the curing of the Matrimid resin, DBA copolymerizes with BMI via the ene-type linear chain extension reaction followed by the Diels–Alder reaction of the intermediate ene reaction product with another DBA at 120–220°C.[1] During curing the increase in MW of the bismaleimide resin initiates phase separation by spinodal decomposition.[31] Morphology of the modified resin depends on modifier MW and content, and the curing conditions, as phase separation competes with gelation or vitrification. In the present modification the curing system would phase-separate at earlier curing stages because the extent of esterification is low at 200°C and the cured resins would have particulate structures with PEP-rich particles dispersed in the bismaleimide matrix, considering the morphologies of the PEP-modified

Matrimid resin (Fig. 3), the higher miscibility of PEP with the bismaleimide matrix, and the morphological results in the modification of epoxies with PEP.[21] At the final stage of curing, where esterification occurs significantly, PEP-rich particles would be incorporated into the matrix by chemical blending to some extent, and some PEP-rich particles would react with phenolic groups of DBA units at the interface between the PEP-rich particles and the bismaleimide matrix, which would enhance the interfacial adhesion. Transesterification at the interface would make the contours of the particles obscure (Fig. 3). Then, in the present modification, the particulate structures of the modified resins would contribute to toughening of the bismaleimide resin, to some extent. The main difference between the present modification system and the modification of the epoxy resin with PEP is the occurrence of esterification in the former system. It is well known that the interfacial adhesion is one of the most important factors in obtaining effective modifiers for improving the brittleness of epoxies.[2]

CONCLUSION

PEP and PEPI (10 mol % IP unit) were effective modifiers for the Matrimid resin. Their effectiveness depended on polyester structure, MW, and content. Three factors would act mainly to improve the brittleness of the Matrimid resin: (1) the reinforcement of the matrix itself by incorporated polyesters, (2) the existence of the relaxations near room temperature, and (3) the two-phase separation structures of the modified resins and the enhancement of the interfacial adhesion between the PEP-rich particles and the matrices by transesterification. The most suitable compositions for the modification of the Matrimid resin were inclusion of 20 wt % of PEP (18,200) and K_{IC} for the modified resin increased 80% with no loss of mechanical properties.

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