

# Modification of Cyanate Ester Resin by Poly(ethylene phthalate) and Related Copolyesters

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**ABSTRACT:** Aromatic polyesters were prepared and used to improve the brittleness of the cyanate ester resin. The aromatic polyesters include poly(ethylene phthalate) (PEP) and poly(ethylene phthalate-co-1,4-phenylene phthalate). The polyesters were effective modifiers for improving the brittleness of the cyanate ester resin. For example, inclusion of 20 wt % PEP (MW 19,800) led to a 120% increase in the fracture toughness ( $K_{IC}$ ) with retention in flexural properties and a slight loss of the glass transition temperature compared to the mechanical and thermal properties of the unmodified cured cyanate ester resin. The microstructures of the modified resins were examined by scanning electron microscopy and dynamic viscoelastic analysis. The thermal stability of the modified resins was lower than that of the unmodified resin as determined by thermogravimetric analysis. The water absorptivity of the modified resin increased significantly, compared to that of the unmodified cured cyanate ester resin. The toughening mechanism was discussed in terms of the morphological and dynamic viscoelastic behaviors of the modified cyanate ester resin system. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 208–219, 2000

**Key words:** cyanate ester resin; modification; poly(ethylene phthalate); poly(ethylene phthalate-co-1,4-phenylene phthalate); fracture toughness

## INTRODUCTION

Cyanate ester resins are among the most important thermosetting polymers and have received attention because of outstanding physical properties and low water absorptivity.<sup>1</sup> In general, the drawback of the thermosets is that they are brittle. The toughening of epoxies has been increased by blending with reactive rubbers such as carboxyl-terminated butadiene-acrylonitrile rubbers<sup>2</sup> or epoxide-containing acrylic elastomers.<sup>3</sup> The use of reactive rubbers leads to a reduction in the mechanical and thermal properties. Furthermore, reactive rubbers are rather less effective in the highly crosslinked epoxies.<sup>3</sup> Recently, modifi-

cations of thermosets with engineering thermoplastics have been studied as alternatives to reactive rubber toughening from the viewpoint of the maintenance of mechanical and thermal properties for the matrix resins. The brittleness of epoxy resins has been improved by blending engineering plastics such as polysulfones (PSFs),<sup>4–6</sup> and poly(ether imide) (PEI).<sup>7–9</sup> Engineering thermoplastics examined as modifiers for the cyanate ester resin include PEI, PSF, poly(ether sulfone), polyarylate, and poly(ether ketone ketone).<sup>10–15</sup> Modification of the cyanate ester resin has been carried out on the basis of information on the toughening of epoxy and bismaleimide resins by thermoplastics in our laboratory.<sup>16–29</sup> For example, poly(ethylene phthalate) (PEP) and related copolyesters are effective modifiers for epoxy<sup>16,22</sup> and bismaleimide resins.<sup>28</sup> Poly(butylene phthalate) (PBP) and related polyesters are also effec-

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tive as modifiers for epoxies<sup>27</sup> and bismaleimide.<sup>29</sup>

This article reports the modification of the cyanate ester resin by aromatic polyesters. The aromatic polyesters include PEP and poly(ethylene phthalate-co-1,4-phenylene phthalate) (PEPP). The effects of structure, molecular weight, and amount of the polyesters on the toughness of the cured resins were examined.

## EXPERIMENTAL

### Materials

The cyanate ester resin was a commercial, bisphenol-A type material (AroCy B 10™, mp 79°C, Ciba Geigy Corp.). PEP was prepared by the reaction of 1,2-ethanediol and phthalic anhydride as reported previously.<sup>22</sup> PEPP was prepared by transesterification of PEP and hydroquinone diacetate. Other reagents were used as received.

### Measurements

<sup>1</sup>H-NMR spectra were recorded on a 90-MHz instrument (JEOL JNM-9MX 90) at 60°C using CDCl<sub>3</sub> as the solvent and tetramethylsilane as the internal standard. The molecular weights of the polyesters were measured by gel permeation chromatography (GPC, Shimadzu LC-5A instrument) using polystyrene standards. 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). 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 glass transition temperatures ( $T_g$ ) of the polyesters were measured as the onset temperatures by differential scanning calorimetry (DSC, Shimadzu DSC 41M) at a heating speed of 10°C/min under nitrogen. The  $T_g$  values of the cured resins were obtained by thermal mechanical analysis (TMA, Shimadzu TMA 40M, penetration mode) at a heating speed of 5°C/min under nitrogen. Scanning electron micrographs (SEMs) 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 at between -50 and 350°C at a heating speed of 5°C/min and a 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

PEP was dissolved in the cyanate ester resin at 120°C without solvents. Then the catalysts (2 phr), composed of copper naphthenate and *p*-nonylphenol (8.5/91.5 wt ratio), were added to the mixture at about 60°C; copper naphthenate contains 8 wt % Cu<sup>2+</sup>. The resulting clean mixture was degassed *in vacuo* at 80°C for 30 min. The mixture was poured into a mold, which was preheated at 100°C, to obtain a 7 mm thick plaque. The mold consisted of one pair of upright stainless plates spaced by a U-shaped silicon rubber stick. The amount (wt %) of the modifier was calculated based on the matrix resin. The curing cycle was 150°C for 1 h, 177°C for 3 h, 210°C for 1 h, and 250°C for 2 h. After curing the oven temperature was decreased from 250 to 50°C at a cooling speed of 25°C/h.

In the PEPP modification copper naphthenate (0.17 phr) alone or copper naphthenate (0.17 phr) and a smaller amount of *p*-nonylphenol (0.61 phr) were used.

### Reaction of Cyanate Ester Resin with Alcohol

The reaction of the cyanate ester resin and triethylene glycol monomethyl ether (TGME) was examined as follows.

One gram of AroCy B 10 (3.6 mmol), 11.82 g of TGME (72 mmol), and 11.8 mg of copper naphthenate were mixed in the absence of *p*-nonylphenol and stirred at 80°C for about 1 h to homogenize the mixtures. The reaction was carried out at 200°C for 1 h without stirring. After the reaction was over the reaction mixtures were diluted with dichloromethane, poured into ice water, and extracted with dichloromethane several times. The dichloromethane solution was washed with water and dried over anhydrous MgSO<sub>4</sub>, and dichloromethane was evaporated. The crude product was dried *in vacuo* at 80°C. The yield was 49%.

## RESULTS AND DISCUSSION

### Characterization of Aromatic Polyesters

In this study various molecular weights of PEP were prepared in quantitative yield by polycondensation of 1,2-ethanediol and phthalic anhydride as reported previously.<sup>22</sup> PEPP was pre-

**Table I** Characterization of PEP and Related Polyesters

Entry No.	Polyester <sup>a</sup> Composition	$M_{\text{GPC}}^{\text{b}}$ ( $10^3$ )	$M_n^{\text{b}}$ ( $10^3$ )	$M_w/M_n$	$T_g^{\text{c}}$ (°C)	A.V. <sup>d</sup> (meq/g)
PEP						
3	—	6.4	4.6	1.6	—	0.069
2	—	9.2	6.2	1.7	26	—
1	—	13.6	8.5	1.8	29	0.048
4	—	14.2	8.9	1.8	—	—
5	—	19.8	12.1	1.9	—	—
6	—	26.7	16.3	1.8	30	—
PEPP						
1	Ph 10	4.8	6.4	1.6	27	—
2	9	8.7	4.2	2.9	—	—

<sup>a</sup> Ph, 1,4-phenylene unit (mol %).<sup>b</sup> By GPC.<sup>c</sup> By DSC.<sup>d</sup> Terminal carboxyl group content.

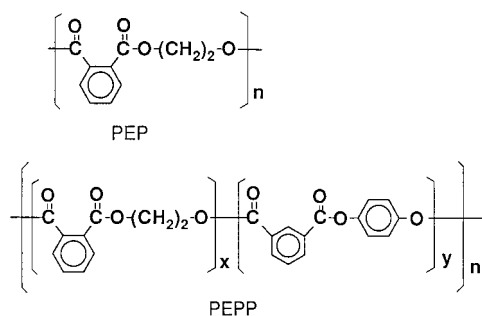
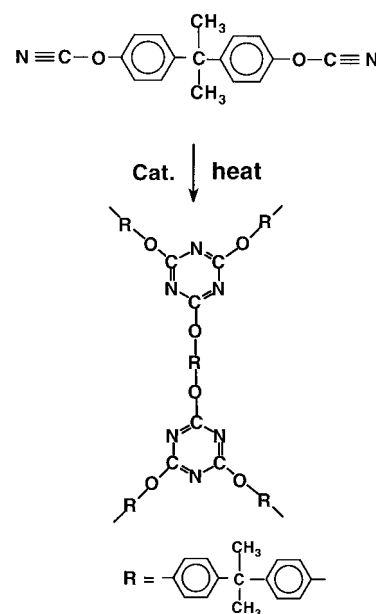
pared by transesterification of PEP and hydroquinone diacetate. Table I reports some characteristic properties of the aromatic polyesters. The structure of the polyesters used are shown in Scheme 1. The GPC average molecular weight ( $M_{\text{GPC}}$ ), based on the peak position in the GPC curve, was used as a measure of the molecular weight (MW) here and in previous articles<sup>16,22,27–29</sup> because the number average molecular weight is highly sensitive to the presence of a small amount of lower MW materials.

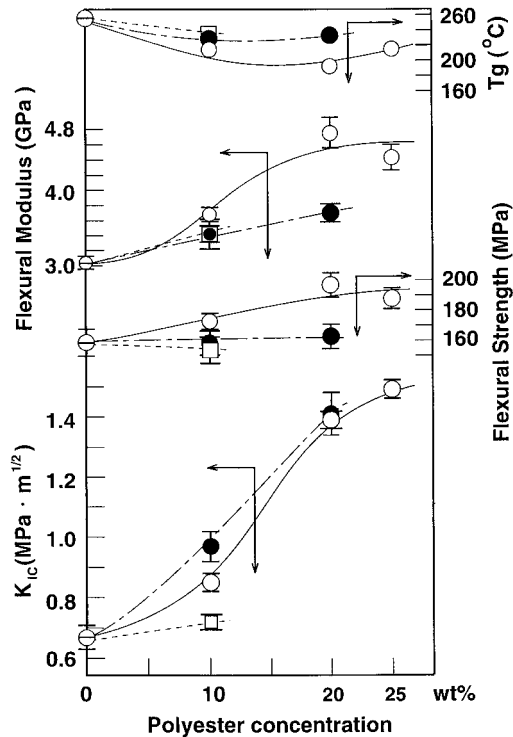
### Mechanical and Thermal Properties of Modified Cyanate Ester Resins

The curing reaction of the cyanate ester resins is cyclotrimerization of the cyanate groups to form highly crosslinked polycyanurate networks (Scheme 2). The curing reaction was slow in the absence of the catalyst but accelerated in the presence of the catalyst composed of phenols and

metal ions.<sup>30</sup> Various kinds of catalyst compositions were shown in the technical report of Rhone-Poulenc Inc.<sup>31</sup> According to the pioneering work of Shimp,<sup>32</sup> the metal ion has a significant effect on the thermal stability at 235°C in air and moisture plasticization (wet heat deflection temperature); the preference is  $\text{Cu}^{2+} = \text{Co}^{2+} > \text{Zn}^{2+} > \text{Mn}^{2+} > \text{Fe}^{3+} > \text{Al}^{3+}$ . So we selected  $\text{Cu}^{+2}$  as a metal ion, considering the preference in the metal ion.

The unmodified cyanate ester resin was transparent. The transparency of the modified resins

**Scheme 1** The structures of the modifiers.**Scheme 2** The cyclotrimerization of the cyanate esters.



**Figure 1** The physical properties of the modified resins as function of modifier concentration: ( $\ominus$ ) control, ( $\square$ ) MW 6400 PEP, ( $\circ$ ) MW 13,600 PEP, and ( $\bullet$ ) MW 26,700 PEP.

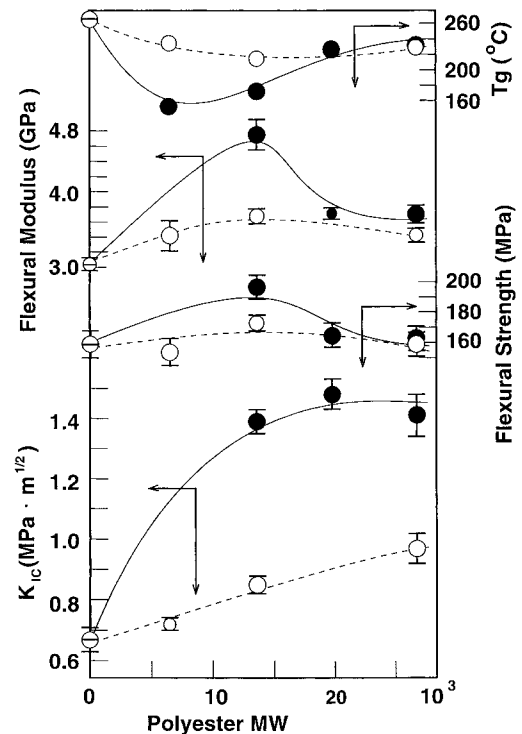
depended on the modifier structure, MW, and content as follows. In the modification of the cyanate ester resin with PEP the modified resin was transparent on 10 wt % inclusion of PEP with an MW of less than 13,600 and became translucent by using 20 wt % of PEP. The modified resins were opaque with the use of more than 20 wt % of PEP having an MW of more than 19,800.

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. The flexural strength and modulus for the modified resins were equal to or larger than those for the unmodified resin. The inclusion of 25 wt % of PEP (MW 13,600) led to a 120% increase in  $K_{IC}$  with an increase in flexural properties. The  $T_g$  values of the modified resins were lower than that of the unmodified resin.

Figure 2 shows the dependence of physical properties of the modified resin on the PEP MW. The  $K_{IC}$  for the modified resins increased with increasing PEP MW on 10 wt % inclusion. When using 20 wt % of PEP with a MW of more than

13,600 the  $K_{IC}$  for the modified resins increased considerably, but their efficiency as modifiers was independent of the PEP MW. Flexural strength for the modified resins was equal to or larger than that for the unmodified resin. Flexural moduli for the modified resins increased significantly on the 20 wt % addition of PEP compared to that for the unmodified resin. When using 20 wt % of the lower MW PEP the  $T_g$  values decreased considerably. It is noteworthy that the test specimen of the cured resin could not be prepared on the 20 wt % inclusion of PEP with an MW of less than 9200 because of the fracture of the resin plaque after curing; this was perhaps because of the occurrence of internal stress on cooling below the  $T_g$  of the cured resin. It is thought that the structure of the matrix itself would be modified by PEP inclusion as shown later in the water absorption tests, dynamic viscoelastic analyses, and a model reaction.

Table II shows the representative results for the modification of the cyanate ester resin with the aromatic polyesters. PEPP has terminal alcoholic and phenolic groups and was also examined as a modifier, considering an increase in water



**Figure 2** The dependence of physical properties for the modified resins on PEP molecular weight: ( $\ominus$ ) control, ( $\circ$ ) 10 wt % addition, and ( $\bullet$ ) 20 wt % addition.

**Table II Physical Properties of Modified Cyanate Resins**

Entry No.	Polyester				$K_{IC}$ (MN/m <sup>3/2</sup> )	$n$	Flexural Properties			
	No. <sup>a</sup>	Composition <sup>b</sup> (mol %)	MW (10 <sup>3</sup> )	Content (wt %)			Strength (MPa)	Modulus (GPa)	$n$	$T_g^c$ (°C)
Control			—	—	0.67 ± 0.04	7	159 ± 9	3.04 ± 0.08	7	248
PEP series <sup>d</sup>										
07	PEP1	—	13.6	10	0.85 ± 0.03	7	173 ± 5	3.68 ± 0.09	8	215
02	PEP1	—	13.6	20	1.39 ± 0.04	6	197 ± 8	4.75 ± 0.20	5	193
08	PEP1	—	13.6	25	1.49 ± 0.04	6	188 ± 7	4.43 ± 0.17	5	216
05	PEP5	—	19.8	20	1.48 ± 0.05	7	165 ± 8	3.71 ± 0.07	7	227
06	PEP6	—	26.7	20	1.41 ± 0.07	5	163 ± 8	3.70 ± 0.12	7	233
PEPP series										
11 <sup>e</sup>	PEPP1	Ph 10	4.8	20	1.04 ± 0.04	7	180 ± 15	4.25 ± 0.09	7	200
12 <sup>e</sup>	PEPP2	9	8.7	20	1.07 ± 0.07	6	178 ± 19	4.30 ± 0.10	5	221
13 <sup>f</sup>	PEPP2	9	8.7	20	1.11 ± 0.06	6	189 ± 13	4.39 ± 0.10	5	222

The ± values are the mean ± the standard deviation;  $n$ , number of specimens tested.

<sup>a</sup> Entry number in Table I.

<sup>b</sup> Ph, 1,4-phenylene unit.

<sup>c</sup> By TMA.

<sup>d</sup> Catalyst system composed of copper naphthenate (0.17 phr) and *p*-nonylphenol (1.83 phr).

<sup>e</sup> Catalyst system containing copper naphthenate (0.17 phr) alone.

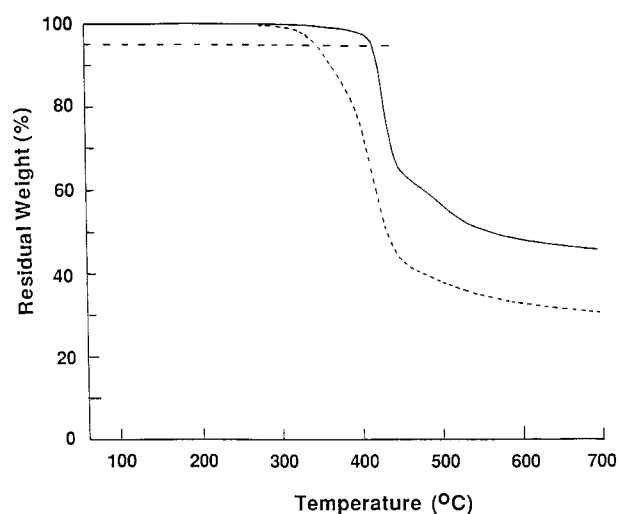
<sup>f</sup> Catalyst system composed of copper naphthenate (0.17 phr) and *p*-nonylphenol (0.61 phr).

absorptivity of the PEP-modified resin as shown below. A smaller or no amount of *p*-nonylphenol was used in the PEPP modification, because the terminal phenolic group of PEPP would act as an accelerator in place of *p*-nonylphenol. The physical properties of PEPP-modified resins did not depend on the amount of *p*-nonylphenol (entries 12, 13). PEPP was less effective as the modifier than PEP.

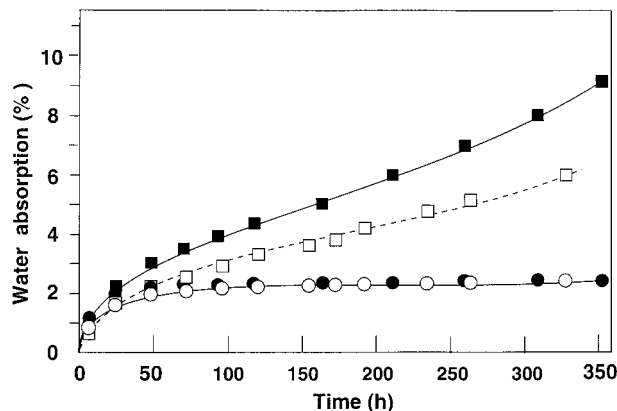
TGA was carried out to examine the thermal stability of the modified resins (Fig. 3). The parent cured cyanate ester resin was stable at high temperature and underwent a weight loss of 5% at 432°C. The thermal stability of the modified resin was lower than that of the unmodified resin: the temperature of a 5 wt % loss was 356°C for the PEP (MW 19,800) 20 wt % modified resin.

One of the characteristics of the cured cyanate ester resin is its low water absorptivity. Water absorption tests were carried out by immersing the cured resins in boiling water to examine the influence of PEP incorporation. Water absorption of the unmodified resin increased with time and then leveled off at less than 2.5 wt % water gain (Fig. 4). Water absorption increased with increasing PEP incorporation. When using 10 wt % of PEP (MW 13,600) the water absorption of the modified resin was similar to that of the unmodified materials. However, water absorption of the

PEP (MW 13,600) 20 wt % modified resins increased extraordinarily with time and did not level off. When using 20 wt % of MW 8700 PEPP as the modifier, the increase in water absorption was suppressed, but no leveling off in the water absorption versus the time curve was observed (Fig. 5). The use of 20 wt % of lower MW PEPP led to a significant increase in water absorption. The



**Figure 3** The thermogravimetric analysis of the unmodified (—) 0 wt % (control) and modified resins: (---) 20 wt % addition PEP (MW 19,800).



**Figure 4** The water absorption of the unmodified (●) 0 wt % (control) and PEP (MW 13,600) modified resins: (○) 10 wt % addition, (□) 20 wt % addition, and (■) 25 wt % addition.

surface of the modified resin whitened gradually with an increase in the extent of water absorption, which perhaps was from hydrolysis. The less the MW of the polyester, the more the content of the terminal hydroxyl groups and the more water absorption, because incorporation of an alcoholic group would inhibit the formation of the polycyanurate network in the cyanate matrix to some extent as shown later in the model reaction of cyanate and alcoholic groups. The difference in water absorptivity between the PEP-modified and PEPP-modified resins also indicates a negative effect of alcoholic groups.

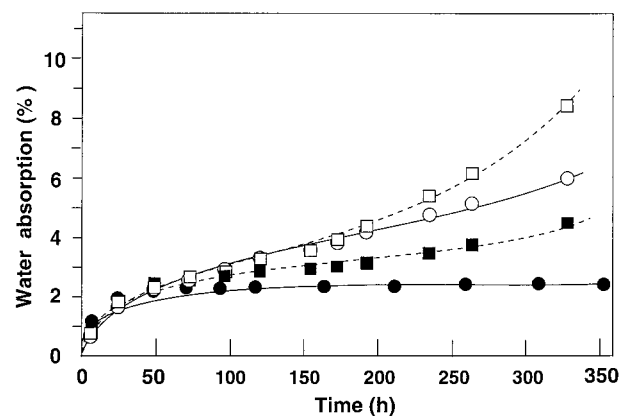
#### Microstructures of Modified Cyanate Ester Resins

The morphologies of the cured resins were investigated by the SEMs. Figure 6 shows SEMs for the unmodified and PEP-modified resins. The unmodified cured cyanate ester resin had only one phase [Fig. 6(A)]. A small amount of fine irregular particles were observed in the fracture surface of the PEP (MW 13,600, 25 wt %) modified resin [Fig. 6(B)]. When using 20 wt % of PEP (MW 19,800), the fracture surface was rough and well-dispersed fine irregular particles ( $<1 \mu\text{m}$ ) were observed [Fig. 6(C)]. The PEP-rich irregular particle size became larger with increasing PEP MW [Fig. 6(D)].

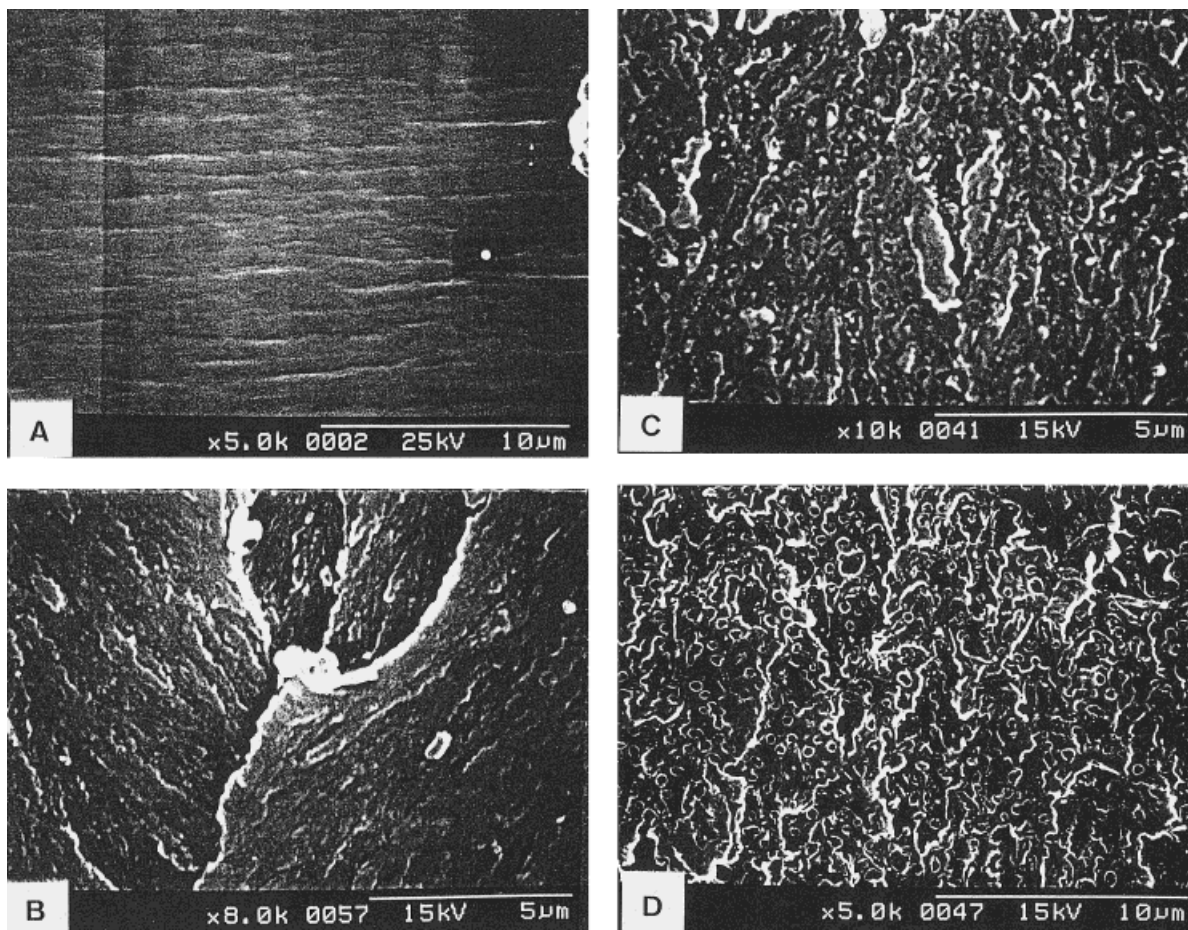
Dynamic viscoelastic analysis can give information on the microstructure of cured resins. Figure 7 shows the storage moduli,  $G'$ , and  $\tan \delta$  curves for the unmodified and PEP-modified resins. The peak position of the  $\alpha$  relaxation in the  $\tan \delta$  curve shifted toward lower temperature

with increasing PEP (MW 13,600) content. Their shape became considerably broader and the magnitude of the  $\tan \delta$  curve increased in the region from room temperature to the  $\alpha$ -relaxation peak temperature compared to dynamic viscoelastic behavior for the cured cyanate ester resin. The broadness of the  $\alpha$  relaxation and the increase in the magnitude of the  $\tan \delta$  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 cyanate ester resin with more than 20 wt % of PEP (MW 13,600) a new relaxation peak ( $\alpha'$  relaxation) was observed at about  $40^\circ\text{C}$  compared to that for the unmodified resin. The appearance of the new  $\alpha'$ -relaxation peak in the  $\tan \delta$  curve indicates the existence of the phase-separated structure for the PEP-modified resin. The storage moduli at room temperature for the modified resin were larger than that for the unmodified resin.

Figure 8 shows the PEP MW dependence of dynamic viscoelastic behaviors of the modified resin on 20 wt % inclusion. With a lower MW (13,600) the  $\alpha$ -relaxation peak position shifted considerably toward a lower temperature, its shape became broader, and the magnitude of the  $\tan \delta$  curve increased in the region from room temperature to the  $\alpha$ -relaxation peak temperature compared to that for the unmodified resin. The peak position and the shape of the  $\alpha$ -relaxation peak were restored to some extent by the use of higher MW PEP and the  $\alpha'$ -relaxation peak appeared at  $40^\circ\text{C}$ . This indicates that the compatibility of PEP and the cyanate ester resin are



**Figure 5** The water absorption of the unmodified (●) 0 wt % (control) and modified resins: (○) 20 wt % addition PEP (MW 13,600), (□) 20 wt % addition PEPP (MW 4800), and (■) 20 wt % addition PEPP (MW 8700).

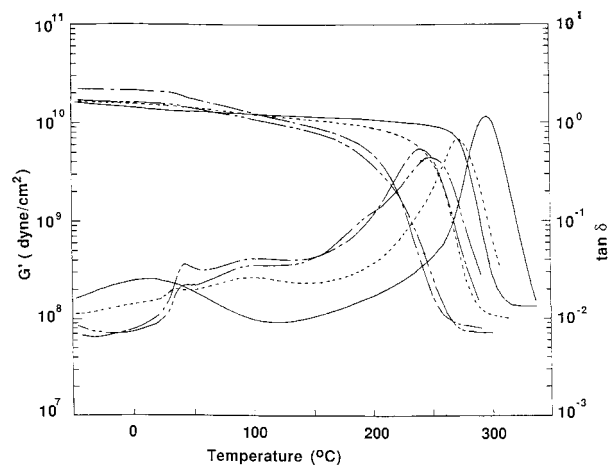


**Figure 6** The SEMs of fracture surfaces for the (A) control and PEP-modified resins: (B) 25 wt % addition (MW 13,600), (C) 20 wt % addition (MW 19,800), and (D) 20 wt % addition (MW 26,700).

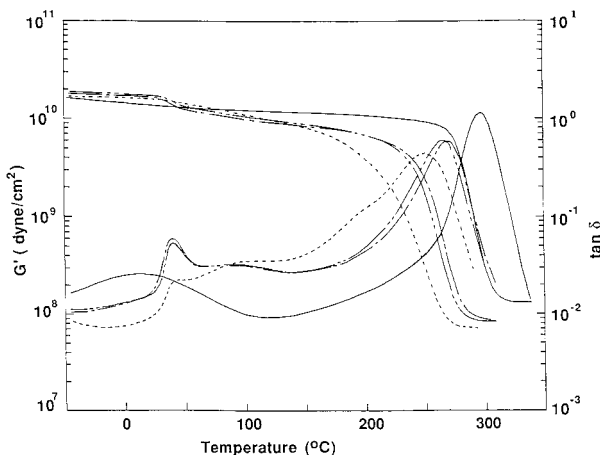
lowered with increasing PEP MW; this behavior corresponds to morphological behavior (Fig. 6). The storage moduli at room temperature for the modified resin were larger than that for the unmodified resin.

#### Model Reaction of Curing in Presence of Modifier

The dynamic viscoelastic analysis of the modified resins indicates the complexity of the matrix structure. Furthermore, the water absorptivity of the modified resin was considerably greater than that of the unmodified resin. In the curing of the cyanate ester resin in the presence of the catalyst, phenols act as curing accelerators and a phenol is liberated after the formation of the triazine ring in the latter stage of curing; the liberated phenol is not necessarily the same as the starting one but is the most acidic one.<sup>33</sup> PEP as the modifier has terminal alcoholic and carboxylic groups and both



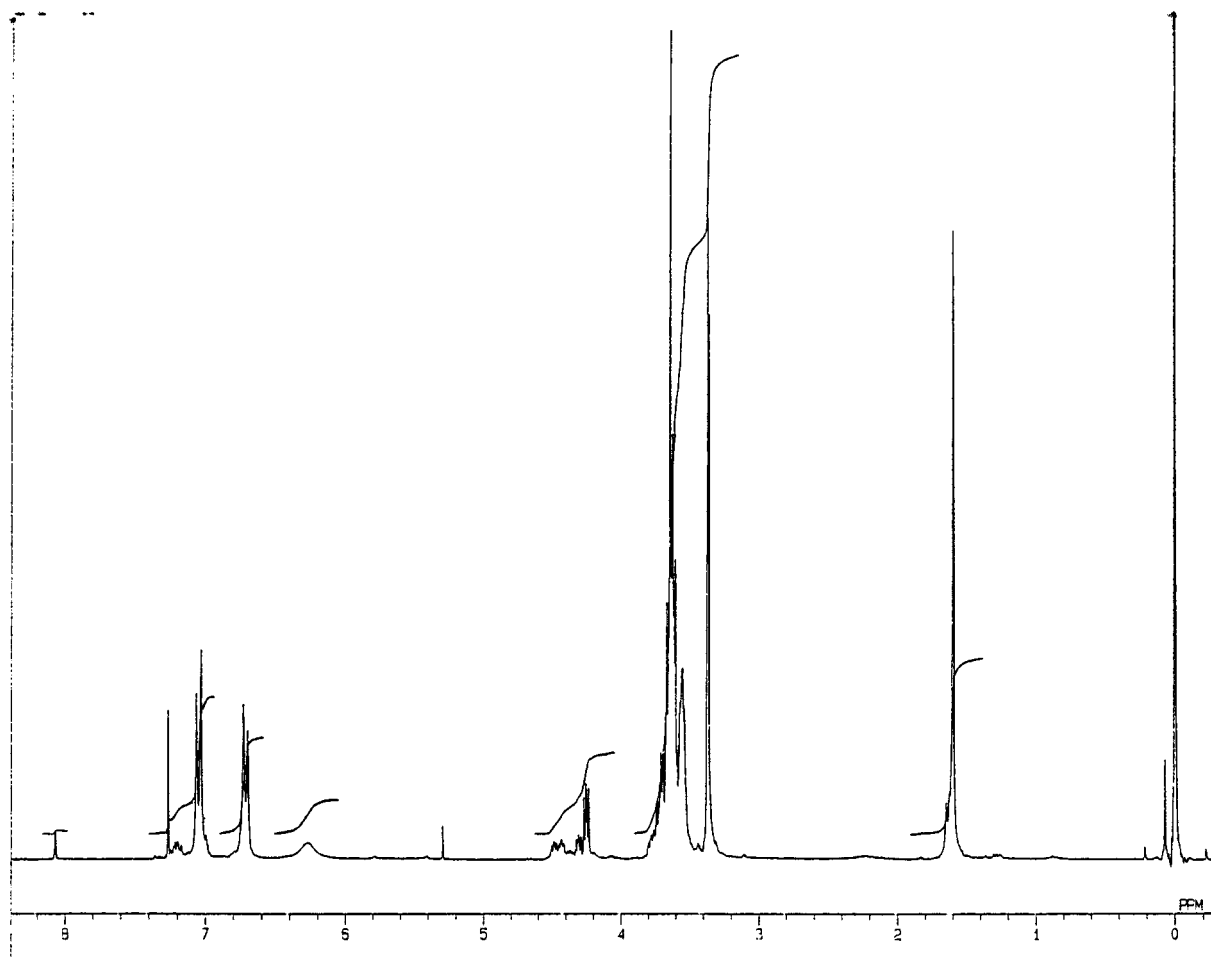
**Figure 7** The dynamic viscoelastic analysis of unmodified (—) 0 wt % (control) and PEP (MW 13,600) modified resins: (---) 10 wt % addition, (— · —) 20 wt % addition, and (— — —) 25 wt % addition.



**Figure 8** The dynamic viscoelastic analysis of unmodified (—) 0 wt % (control), and PEP (20 wt % addition) modified resins: (---) MW 13,600, (— · —) MW 19,800, and (— — —) MW 26,700.

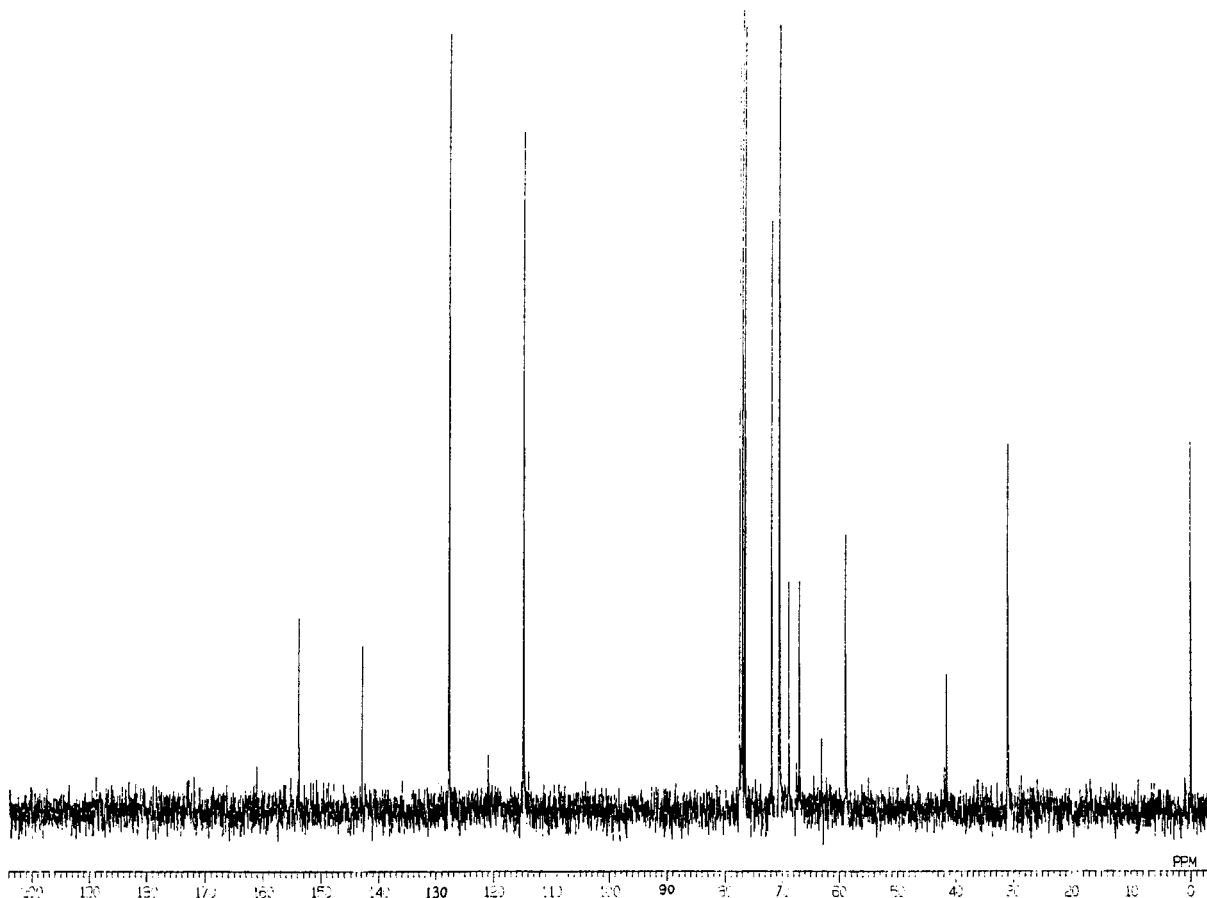
groups will act as accelerators in the present modification. Carboxylic groups will be liberated after curing, but alcoholic groups might be difficult to liberate and interfere with the formation of the triazine ring, because the acidity of the alcoholic groups was much smaller than that of the phenolic ones. To examine the effect of the terminal alcoholic group on curing, the model reaction was carried out by the reaction of cyanate ester and TGME in the presence of copper naphthenate as the catalyst; to avoid crosslinking the reaction was carried out in a large excess of TGME (TGME/cyanate ester resin in a 10/1 equivalent ratio) at 200°C for 1 h without solvents. The reaction product was analyzed by <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, and IR spectra.

Figure 9 shows a <sup>1</sup>H-NMR spectrum of the reaction product; the proton signals based on methyl, methoxy, oxyethylene, and aryl groups are observed at 1.60, 3.37 and 3.38, 3.54–3.72,



**Figure 9** The <sup>1</sup>H-NMR spectrum of the reaction product with CDCl<sub>3</sub> as the solvent.



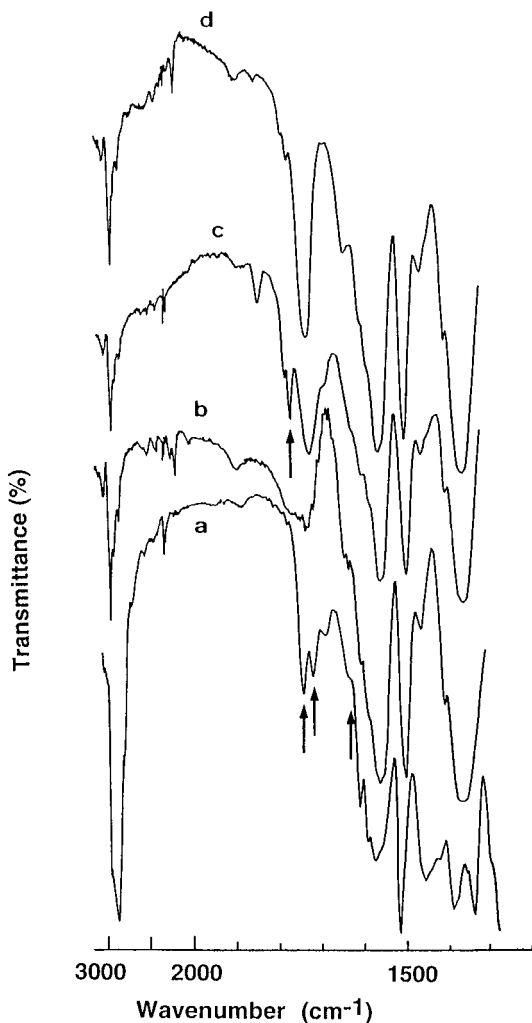


**Figure 10** The  $^{13}\text{C}$ -NMR spectrum of the reaction product with  $\text{CDCl}_3$  as the solvent.

and 6.70–7.07 ppm, respectively, and the broad peak at 6.27 ppm is thought to be based on the N—H proton. Figure 10 shows the  $^{13}\text{C}$ -NMR spectrum of the reaction product: the carbon signal (109 ppm) based on the cyanate group and that (174 ppm) of the triazine ring<sup>34</sup> cannot be observed. The carbon signals at 161.1 and 153.8 ppm are thought to be based on iminocarbonate and carbamate groups, respectively; in the model reaction of curing in solution using *p*-*tert*-butylphenyl cyanate the carbon signals of the iminocarbonate and the carbamate groups from the reaction of the cyanate group with water (contaminant) appeared at 159.5 and 156 ppm.<sup>34</sup>

Figure 11 shows IR spectra of the model reaction product and the cured resins. In the IR spectrum of the model reaction product the signal of the cyanate group at  $2273\text{ cm}^{-1}$  disappeared and the signals at  $1565$  and  $1365\text{ cm}^{-1}$  corresponding to the triazine ring and cyanurate stretching vibrations, respectively, was not observed (Fig. 11,

curve a). Characteristic absorption peaks appeared at  $1575$  and  $1515\text{ cm}^{-1}$  based on the phenyl group. Furthermore, other characteristic absorption peaks were observed at  $1747$  and  $1725\text{ cm}^{-1}$ , which is thought to be based on the carbamates: the former corresponds to primary carbamate based on the reaction of the cyanate group with water and the latter secondary one is based on TGME.<sup>35</sup> The absorption of the iminocarbonate group appeared at  $1640\text{ cm}^{-1}$  (shoulder). The absorption at  $1650\text{ cm}^{-1}$  was observed distinctly together with the absorptions at  $1747$  and  $1725\text{ cm}^{-1}$  in a preliminary experiment ( $100^\circ\text{C}$ , 24 h); the absorption peak of the iminocarbonate group was observed at  $1670\text{ cm}^{-1}$  in the model reaction of curing using *p*-cumyl phenyl cyanate.<sup>36</sup> The results indicate that the reaction of TGME or water and the cyanate group proceeded via the addition to form the iminocarbonate groups that rapidly isomerized into carbamate groups at  $200^\circ\text{C}$  without the formation of the triazine ring (Scheme 3).



**Figure 11** The IR spectra: (curve a) the reaction product, (curve b) the unmodified cured resin, (curve c) the cured resin modified with 20 wt % PEP (MW 6400), and (curve d) the cured resin modified with 20 wt % PEP (MW 26,700).

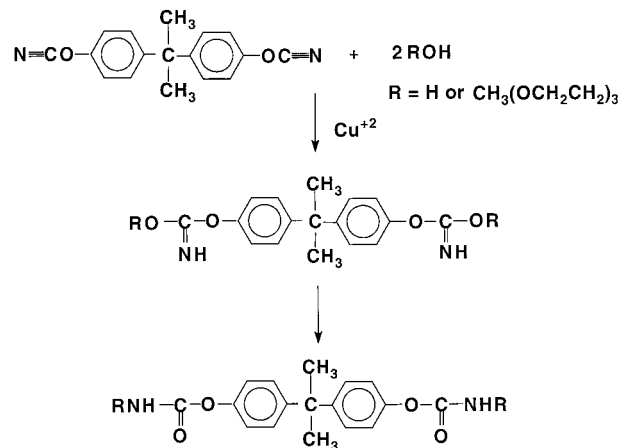
The model reaction of the cyanate ester resin and TGME was carried out in the presence of an excess of TGME to avoid crosslinking. In the curing process the steric constraints based on the 3-dimensional crosslinked structure prevent the formation of an iminocarbonate structure, but some amount of the cyanate ester resin and the polyesters located in the neighborhood would react with each other. IR spectra also gave information on the microstructure of the PEP-modified resins (Fig. 11, curves b–d). A new absorption at  $1775\text{ cm}^{-1}$  appeared in the IR spectra of the PEP-modified resins compared to the parent resin. When using a lower MW PEP the absorption at  $1775\text{ cm}^{-1}$  was stronger than that for the higher

MW PEP-modified material because of the increase in terminal hydroxyl group content of the lower MW PEP; the plaque of the former resin could not be prepared because of fracture in the curing process as described above. Therefore, the matrix compositions will change as shown in the dynamic viscoelastic behavior of the modified resins (Figs. 5, 6). The lack of leveling off in the water absorption versus time curve would perhaps be because of hydrolysis of the iminocarbonate and carbamate structures.

### Toughening Mechanism

The aromatic polyesters used were soluble in the cyanate ester resin without solvents and effective as modifiers for the cyanate ester resin. When using 20 wt % of PEP (MW 19,800) the  $K_{IC}$  for the modified resin increased 120% with retention in flexural properties and a slight loss of  $T_g$  compared to those of the unmodified cured cyanate ester resin. The efficiency of the PEPP was less than that of the PEP.

PEP and related copolyesters were effective modifiers for the highly crosslinked epoxy matrix ( $T_g$ ,  $180^\circ\text{C}$ ) composed of bisphenol-A diglycidyl ether (DGEBA) and 4,4'-diaminodiphenyl sulfone (DDS) and the toughening mechanism was discussed in detail in the literature.<sup>22</sup> In the modification with PEP and related copolyesters the toughening of epoxies could be attained by the particulate structures of the modified resins, and three factors would act mainly to improve the brittleness of the epoxies: the reinforcement of the matrix itself by incorporating the modifier, the high extent of dispersion of the modifier-rich particles, and the existence of the relaxation near



**Scheme 3** The model reaction process.

room temperature. PBP and related copolyesters were also effective modifiers for the DDS-cured DGEBA resin.<sup>27</sup> The toughening mechanism in the PBP modification system is similar to that in the modification with PEP.

In the present modification system the modified cyanate ester resins had particulate structures with PEP-rich irregularly shaped particles less than 1  $\mu\text{m}$  in diameter dispersed in the cyanate-rich matrix. The morphological behavior in the modification of the cyanate with the polyesters can be explained in terms of solubility parameter (SP). The SP values  $[(\text{MJ}/\text{m}^3)^{1/2}]$  for the cyanate ester resin, PEP, and PEPP are 25.23, 25.40, and 25.52, respectively (by Fedors' method<sup>37</sup>). The SP values indicate high miscibility of the aromatic polyesters with the cyanate matrix. Furthermore, the chemical reaction of cyanate and hydroxyl groups would enhance interfacial adhesion and then the miscibility of the polyester with the cyanate matrix. Interfacial adhesion by the chemical reaction would make the contours of the particles irregular [Figs. 6(C,D)]. Dynamic viscoelastic analysis also indicated that the polyesters would dissolve into the matrix to a considerable extent as shown in the broadening of the  $\alpha$ -relaxation peak and the existence of the relaxation in the region from room temperature to the  $\alpha$ -relaxation peak temperature in the  $\tan \delta$  curves (Figs. 7, 8). 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 and in the modification of epoxies with the aromatic polyesters.<sup>22,27</sup>

The existence of the relaxation peak near room temperature is also important to improve the brittleness of the thermosetting polymers. Ochi et al. reported that the presence of the  $\beta$ -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.<sup>38,39</sup> We also reported that several relaxations at more than 50°C contribute to toughening of epoxies in the modification of the DDS-cured DGEBA resins with butyl acrylate-glycidyl acrylate copolymers.<sup>40</sup> Recently, we reported that the existence of the relaxations near room temperature is important to improve the brittleness of epoxies in the modification of the DDS-cured DGEBA resins with PEP, PBP, and related copolyesters.<sup>22,27</sup> In the present modification the  $\alpha'$ -relaxation peak was observed and the magni-

tude of the  $\tan \delta$  curve underwent a considerable increase from room temperature to the  $\alpha$ -relaxation temperature, which is thought to be because of an overlapping of various small relaxations based on the polyester incorporation into the cyanate matrix. These relaxations are effective in toughening the cured cyanate ester resins.

In the modification of epoxies with PEP the modified resins have particulate morphologies with well-dispersed PEP-rich particles dispersed in the matrix. During curing the increase in molecular weight of the cyanate ester resin initiates phase separation by spinodal decomposition.<sup>41</sup> In the present modification the particulate structures of the modified resins contribute to toughening of the cyanate ester resin.

Hence, the toughening mechanism in the present modification is similar to that in the epoxy modification with PEP. The main difference in the present modification system and in the modification of the epoxy resin with the aromatic polyesters is the improvement in interfacial adhesion by the chemical reaction in the former system. It is well known that interfacial adhesion is one of the most important factors to obtain effective modifiers for improving the brittleness of epoxies.<sup>2</sup> However, the existence of the alcohol groups led to the increase in water absorption because of the change in the structure of the cyanate matrices in the present modification.

## CONCLUSION

The aromatic polyesters were effective modifiers for the cyanate ester resin. Three factors acted to improve the brittleness of the cyanate ester resin: the reinforcement of the matrix itself by incorporated polyesters, the existence of the relaxations near room temperature, and the two-phase separation structures of the modified resins and the enhancement of the interfacial adhesion between the modifier-rich particles and the matrices. Inclusion of 20 wt % PEP (MW 19,800) led to a 120% increase in  $K_{IC}$  with retention in flexural properties and a slight loss of  $T_g$  compared to those of the unmodified cured cyanate ester resin. The main disadvantage in the present modification system is the decrease in thermal stability and the increase in water absorptivity.

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