

# Toughening of Cyanate Ester Resin by N-Phenylmaleimide–Styrene Copolymers

TAKAO IJIMA, TAKANORI MAEDA, 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:** The N-phenylmaleimide–styrene copolymer (PMS) was prepared and used to improve the brittleness of the cyanate ester resin. PMS was an effective modifier for improving the brittleness of the resin. The morphologies of the modified resins depended on PMS molecular weight and content. The most effective modification of the cyanate ester resin was attained because of the cocontinuous phase structure of the modified resin. Inclusion of 10 wt % PMS ( $M_w$  133,000) led to an 160% increase in the fracture toughness ( $K_{IC}$ ) for the modified resin with a slight loss of flexural strength and retention of flexural modulus and the glass transition temperature, compared to the values for the unmodified resin. Low water absorptivity of the parent-cured resin was not deteriorated by modification. The toughening mechanism was discussed in terms of the morphological and dynamic viscoelastic behaviors of the modified cyanate ester resin system. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 2931–2939, 1999

**Key words:** cyanate ester resin; modification; N-phenylmaleimide–styrene copolymer; fracture toughness; morphology

## INTRODUCTION

Cyanate ester resins are among the most important thermosetting polymers, and have received attention because of their 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> and 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, modifications of thermosets with engineering thermoplastics have been studied as al-

ternatives 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 (PSF)<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>16–31</sup> For example, poly(ethylene phthalate) (PEP) and related copolyesters were effective modifiers for epoxy<sup>16,22</sup> and bismaleimide resins.<sup>29</sup> Most recently, we examined PEP and related copolyesters as modifiers for cyanate ester resin.<sup>31</sup> PEP was an effective modifier for improvement in toughness, but low water absorptivity of the parent resin was deteriorated because of

Correspondence to: T. Iijima.

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**Table I** Preparation and Characterization of PMS<sup>a</sup>

Entry No.	C <sub>12</sub> H <sub>25</sub> SH <sup>b</sup> (mol %)	Yield (%)	M <sub>w</sub> <sup>c</sup> (10 <sup>4</sup> )	M <sub>w</sub> /M <sub>n</sub>	T <sub>g</sub> <sup>d</sup> (°C)
PMS 25	0.20	—	8.5	2.43	221
26	0.20	95.9	12.9	2.80	225
23	0.20	94.9	13.3	2.91	224
24	0.12	94.8	18.9	3.06	226
22	0.03	92.9	33.2	3.24	226

<sup>a</sup> Feed composition, PMI : St 1 : 1 mol ratio; in acetone at 60°C.

<sup>b</sup> Chain-transfer agent.

<sup>c</sup> By GPC.

<sup>d</sup> By DSC.

the change in the structure of the cyanate matrices.

N-phenylmaleimide–styrene copolymers (PMSs) were effective modifiers for both epoxy<sup>19–21,23–25</sup> and bismaleimide resins.<sup>26,27</sup> Based on such information, we used PMS as a modifier of the cyanate ester resin in this study. The effects of molecular weight and amount of PMS used 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.). N-phenylmaleimide (PMI) was provided by Nippon Shokubai Corp. (Osaka, Japan) and used as received. Styrene (St) was purified by distillation *in vacuo*. PMS was prepared by the radical copolymerization of St and PMI as reported previously.<sup>19</sup> Other reagents were used as received.

### Measurements

<sup>1</sup>H-NMR spectra were recorded on a 90 MHz instrument (JEOL JNM-9MX 90, Tokyo, Japan) at 60°C using CDCl<sub>3</sub> as solvent and tetramethylsilane as internal standard. The molecular weights of PMS were measured by gel permeation chromatography (GPC) (Shimadzu LC-5A instrument, Kyoto, Japan) 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 as a crosshead speed of 1 mm/min (ASTM E-399). The glass transition temperatures ( $T_g$ 's) of PMS were measured as the onset temperatures by differential scanning calorimetry (Shimadzu DSC 41M type) at a heating speed of 10°C/min under nitrogen. The  $T_g$  values of the cured resins were obtained by thermal mechanical analysis (Shimadzu TMA 40M type, the penetration mode) at 5°C/min under nitrogen. Scanning electron micrographs (SEMs) were taken with a combined microanalyzer (JEOL, JXA-8900RL, Tokyo, Japan) using failed specimens in the  $K_{IC}$  tests. Dynamic viscoelastic analysis was performed with a Rheometrics RDS-II type (Rheometrics Co., Tokyo, Japan) between –50 and 350°C at a heating speed of 5°C/min at frequency of 1 Hz.

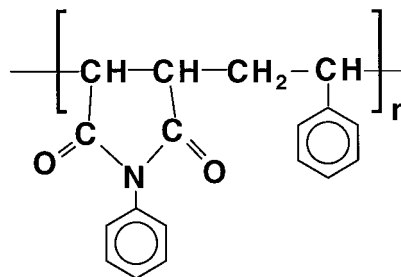
### Curing Procedure

The PMSs were dissolved into 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), was added to the mixture at ca. 80°C: copper naphthenate contains 8 wt % Cu<sup>2+</sup>. The resulting clean mixture was degassed *in vacuo* at 80°C for 15 min. The mixture was poured into a mold, preheated at 100°C, to obtain 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/1 h + 177°C/3 h + 210°C/1 h + 250°C/2 h. After curing, the oven temperature was decreased from 250 to 50°C at a cooling rate of 25°C/h.

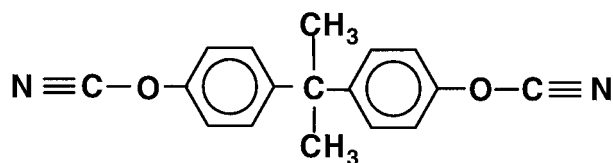
## RESULTS

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

In this study PMSs having various molecular weights were prepared in quantitative yield by



**Scheme 1** Structure of PMS.



Scheme 2 Structure of cyanate ester resin.

radical copolymerization of St and PMI as reported previously.<sup>19</sup> The molecular weight ( $MW$ ) of PMS could be controlled by using dodecanethiol as a chain transfer agent. It is well known that the radical polymerization of St and PMI gives alternating copolymers.<sup>32</sup> Despite the carbon-carbon single bond repeating units, PMS has a high  $T_g$  of ca. 220°C. The weight-average molecular weight ( $M_w$ ) was used as a measure of the molecular weight ( $MW$ ). Table I reports some characteristic properties of PMS. The structure of PMS is shown in Scheme 1.

The unmodified cyanate ester resin was transparent: the structure of the cyanate ester resin is shown in Scheme 2. The transparency of the modified resins decreased with increasing PMS  $MW$  and concentration. The modified resin was transparent on 15 wt % inclusion of PMS with  $M_w$  less than 133,000 and became translucent by using 10 wt % of PMS with  $M_w$  189,000 or  $MW$  332,000. Table II shows the representative results for the modification of the cyanate ester resin with PMS.

Figure 1 shows the mechanical and thermal properties of the modified resins as a function of PMS concentration. In this paper, PMS 23 and 26 were used as equivalent modifiers (Table I). The  $K_{IC}$  for the modified resins increased abruptly on

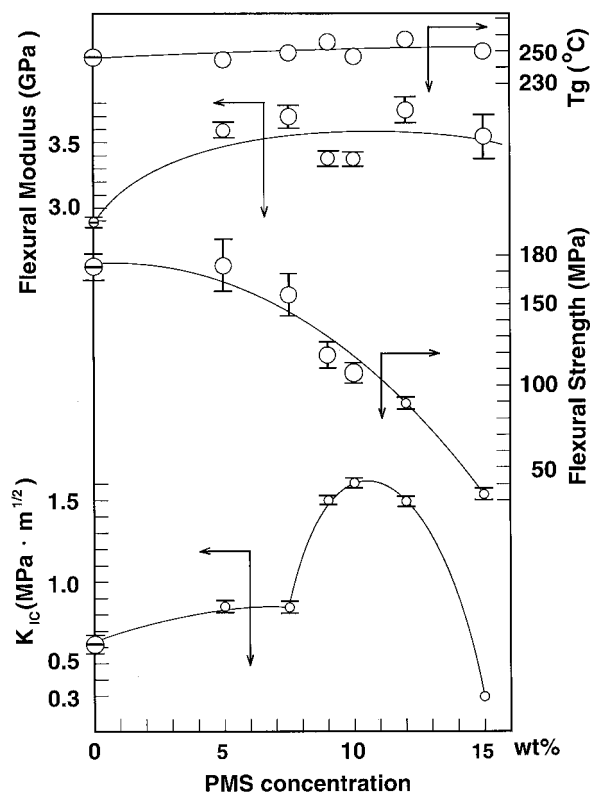


Figure 1 Physical properties of the modified resins as a function of PMS concentration.  $\ominus$ , control;  $\circ$ , PMS ( $M_w$  129,000 or 133,000).

PMS 9–12 wt % inclusion and decreased on a further increase in inclusion. Flexural strength decreased gradually with increasing PMS concentration. Flexural moduli for the modified resins were larger than the value for the unmodified resin. The  $T_g$  values of the modified resins were comparable to the  $T_g$  of the unmodified resin.

Table II Physical Properties of Modified Cyanate Ester Resins<sup>a</sup>

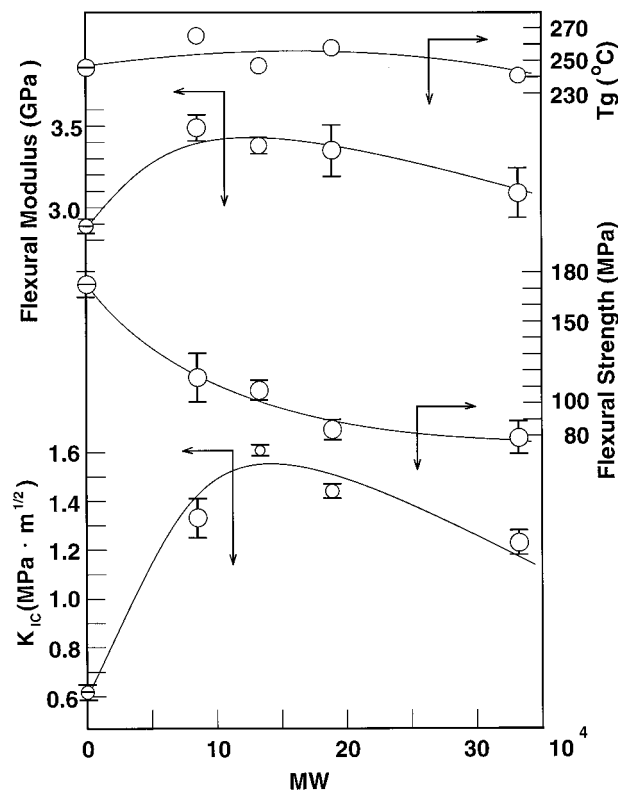
Entry No.	PMS			$K_{IC}$ ( $MN/m^{3/2}$ )	$n^c$	Flexural Properties			$T_g^d$ (°C)
	No. <sup>b</sup>	$MW$ ( $10^4$ )	Content (wt %)			Strength (MPa)	Modulus (GPa)	$n^c$	
Control	—	—	—	$0.62 \pm 0.05$	9	$173 \pm 8$	$2.89 \pm 0.03$	9	246
CP07	PMS25	8.5	10	$1.33 \pm 0.08$	7	$116 \pm 15$	$3.49 \pm 0.08$	6	265
CP10	PMS26	12.9	9	$1.50 \pm 0.02$	7	$119 \pm 8$	$3.38 \pm 0.05$	7	256
CP04	PMS23	13.3	10	$1.61 \pm 0.02$	7	$108 \pm 6$	$3.38 \pm 0.05$	7	250
CP11	PMS26	12.9	12	$1.49 \pm 0.03$	7	$89 \pm 3$	$3.75 \pm 0.10$	7	257
CP05	PMS24	18.9	10	$1.44 \pm 0.03$	5	$84 \pm 6$	$3.35 \pm 0.16$	7	258

<sup>a</sup> The  $\pm x$  values show standard deviation.

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

<sup>c</sup> Number of specimens tested.

<sup>d</sup> By TMA.



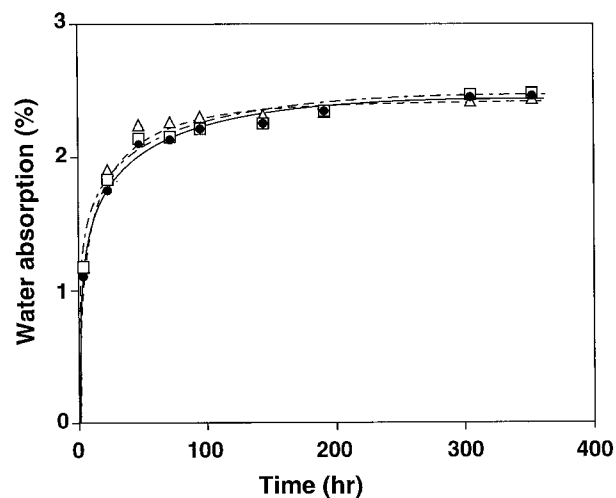
**Figure 2** Dependence of physical properties for the modified resins on PMS molecular weight.  $\ominus$ , control;  $\square$ , 10 wt % PMS addition.

Figure 2 shows the dependence of physical properties of the modified resin on PMS MW. The  $K_{IC}$  for the modified resins increased with an increase in PMS MW up to ca. 150,000 on 10 wt % inclusion and then decreased. When using 10 wt % of PMS with  $M_w$  133,000, the  $K_{IC}$  for the modified resins increased 160%, compared to that for the unmodified resin. Flexural strength for the modified resins decreased with increasing PMS MW. Flexural moduli for the modified resins increased significantly on 10 wt % addition of PMS, compared to the value for the unmodified resin. The  $T_g$  values of the cured resins were not deteriorated by blending PMS.

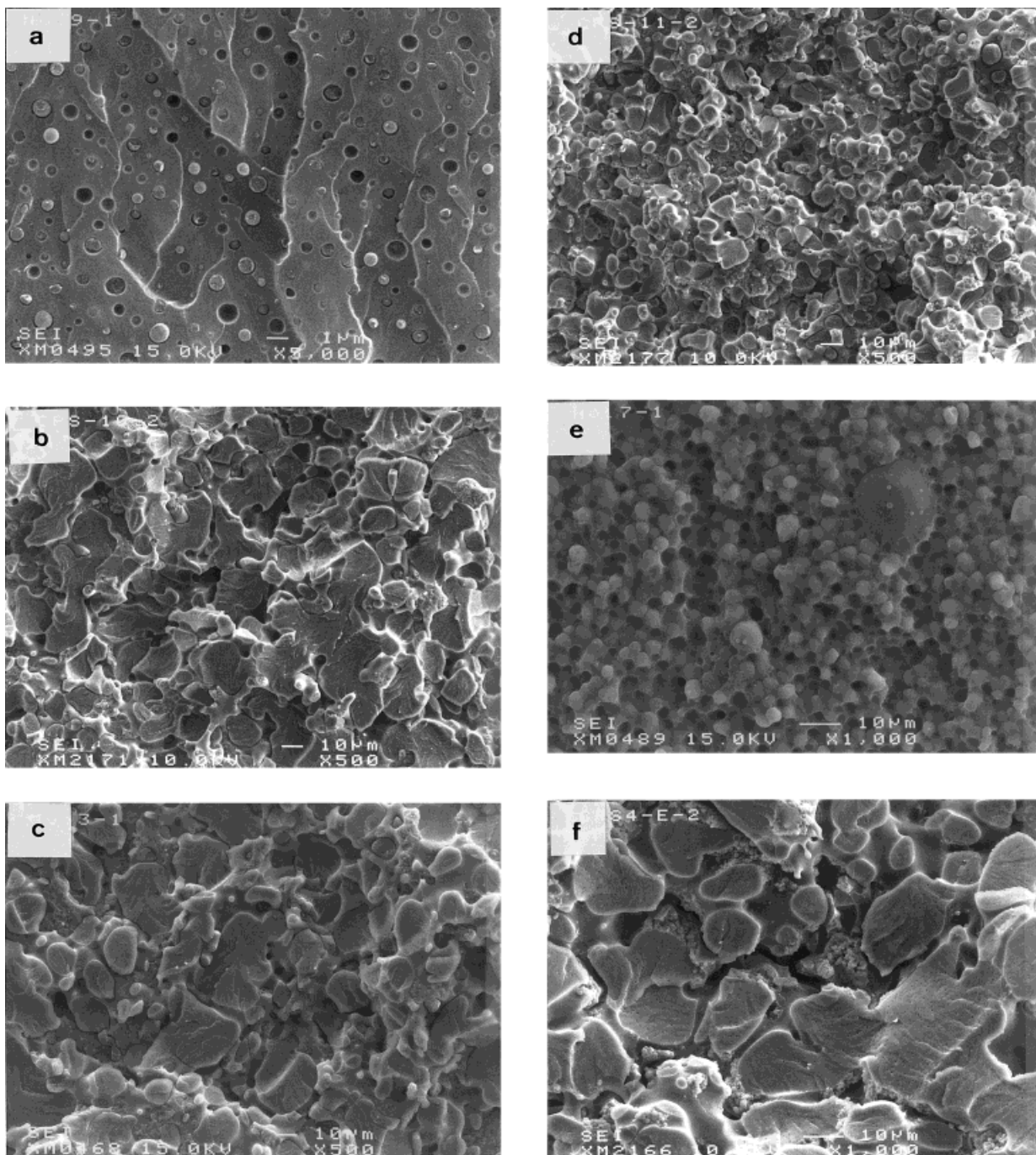
One of the characteristics of the cured cyanate ester resin is its low water absorptivity. Water absorption tests were carried out by immersing the cured resins in boiling water to examine the influence of PMS incorporation. Water absorption of the unmodified resin increased with time and then leveled off at less than 2.5 wt % water gain (Fig. 3). Water absorptivity did not change with PMS incorporation.

### Microstructures of the Modified Cyanate Ester Resins

The morphologies of the cured resins were investigated by the SEMs. Figures 4 and 5 show SEMs for the unmodified and PMS-modified resins. The unmodified cured cyanate ester resins had only one phase as reported previously.<sup>31</sup> Inclusion of PMS led to phase separation. The morphologies of the cured resins changed drastically, depending on PMS MW and concentration. Figure 4 shows a change in morphology with increasing PMS concentration. When using 7.5 wt % of PMS with  $M_w$  133,000, the modified resin had a particulate structure having PMS-rich particles (ca. 0.5  $\mu\text{m}$  in the average diameter) dispersed in the cyanate ester-rich matrix [Fig. 4(a)]. The morphology of the modified resin became a cocontinuous phase structure on 9–10 wt % addition of the same modifier and the morphologies were very similar each other [Figs. 4(b) and 4(c)]. When using 12 wt % PMS, the cured resin also had the cocontinuous phase morphology and the extent of dispersion of the phases became greater [Fig. 4(d)]. On 15 wt % addition of PMS, the morphology further changed and a phase-inverted structure was observed [Fig. 4(e)]. Solvent-etched surfaces were also observed by SEMs to examine the interfacial adhesion between the PMS-rich phase and the cyanate ester matrix. The PMS-rich phases were removed by etching with THF (room temperature, 3 days): part of the PMS-rich phases remain adhered to



**Figure 3** Water absorption of the unmodified and PMS-modified resins.  $\bullet$ , 0 wt % (control);  $\square$ , PMS ( $M_w$  133,000) 10 wt % addition;  $\triangle$ , PMS ( $M_w$  189,000) 10 wt %.

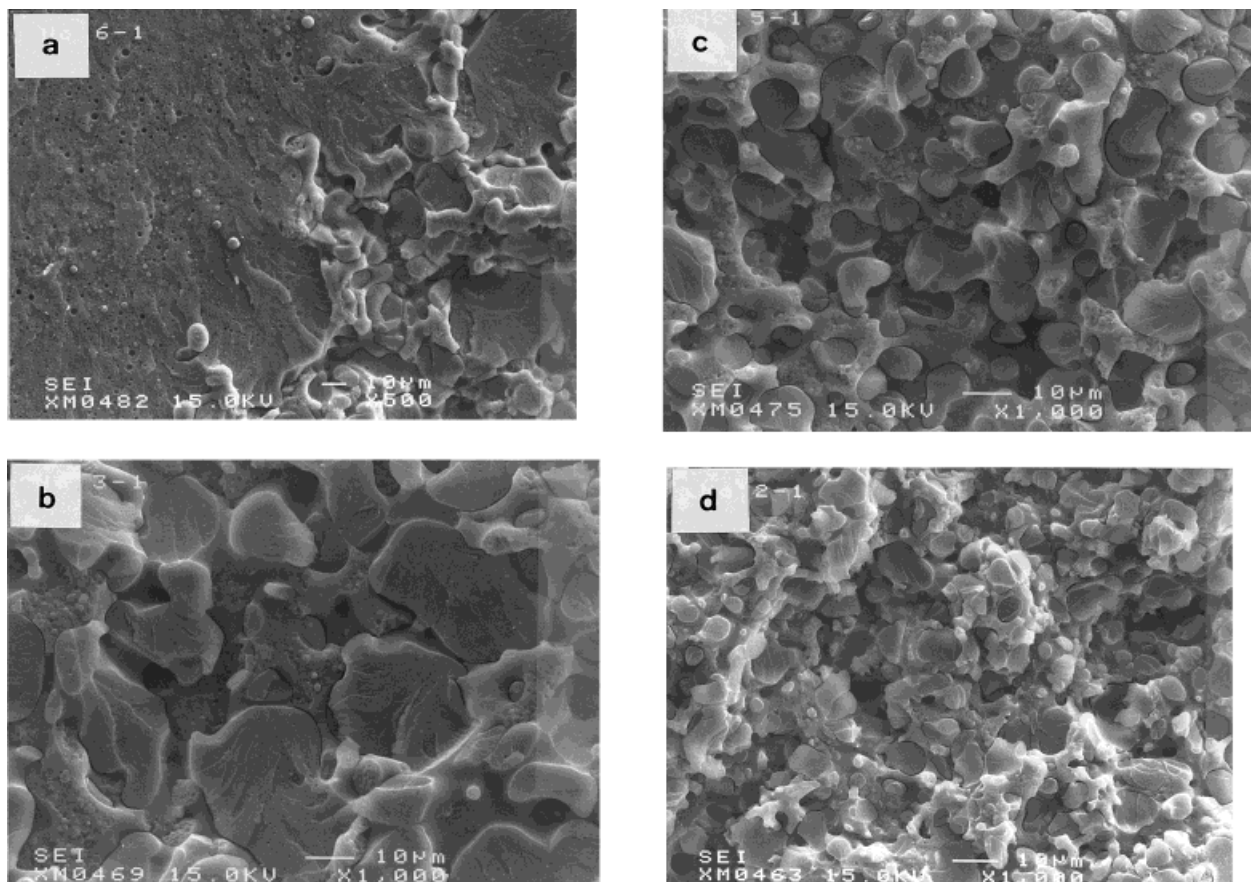


**Figure 4** SEMs of fracture surfaces for the PMS ( $M_w$  133,000) modified resins. Amount of PMS (in wt %): (a) 7.5, (b) 9, (c) 10, (d) 12, (e) 15, and (f) 10, after etching.

the cyanate matrix, and the surface of partially etched PMS-rich phase reveals that the PMS-rich phase is a cluster of PMS-rich small particles [Fig. 4(f)].

When using 10 wt % of PMS with  $M_w$  85,000, the morphology of the modified resin was inter-

mediate between a particulate structure and a cocontinuous phase: part of PMS-formed particles and light PMS-rich continuous phases were also observed [Fig. 5(a)]. The modified resin had cocontinuous phase morphology with 10 wt % inclusion of PMS with  $M_w$  133,000 [Fig. 5(b)]. The



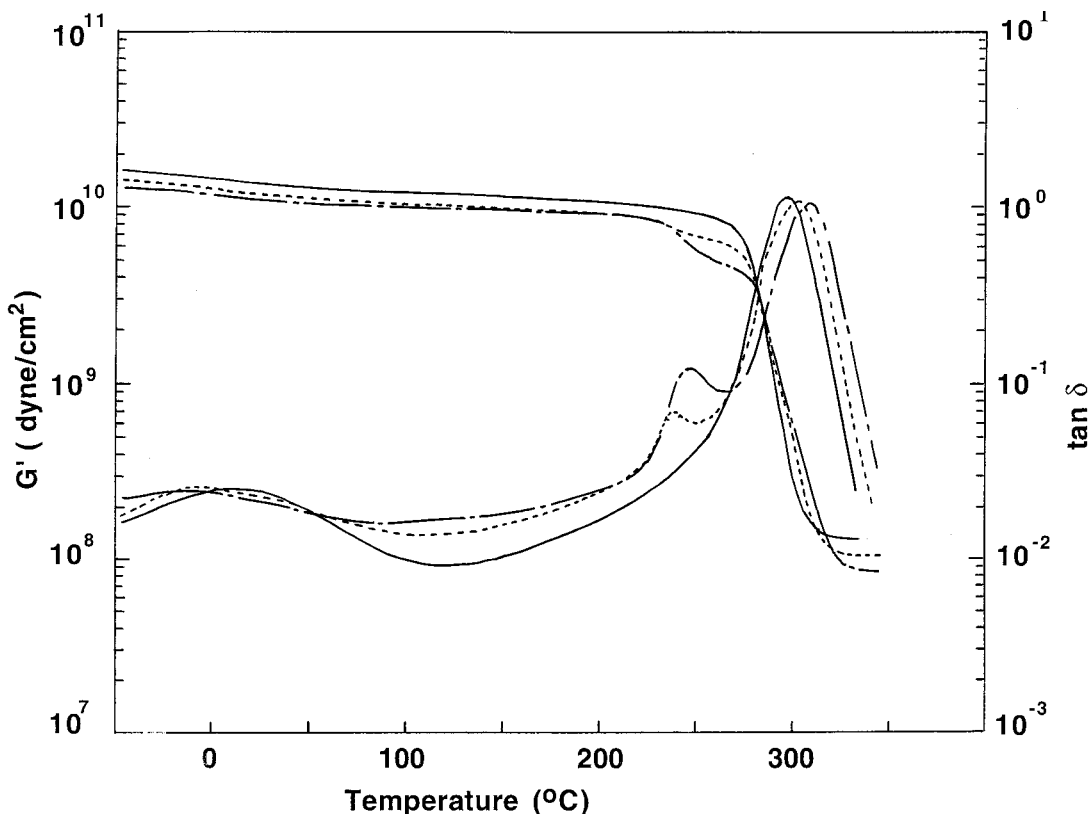
**Figure 5** SEMs of fracture surfaces for the PMS-modified resins. PMS 10 wt % addition.  $M_w$  of PMS: (a) 85,000, (b) 133,000, (c) 189,000, and (d) 332,000.

extent of dispersion of cocontinuous phase became greater with blending higher  $M_w$  (189,000) PMS [Fig. 5(c)]. The modified resin had an intermediate morphology between a cocontinuous phase and phase inversion on 10 wt % incorporation of higher  $M_w$  (332,000) PMS [Fig. 5(d)].

Dynamic viscoelastic analysis can give information on the microstructure of cured resins. Figure 6 shows the storage moduli  $G'$  and  $\tan\delta$  curves for the unmodified and PMS ( $M_w$  133,000) modified resins. The peak position of the  $\alpha$ -relaxation in the  $\tan\delta$  curve shifted slightly toward higher temperature with increasing PMS concentration. Their shape became slightly broader, compared to dynamic viscoelastic behavior for the cured cyanate ester resin. In the modification of the cyanate ester resin with 7.5 wt % of PMS, a new relaxation peak ( $\alpha'$ -relaxation) was observed at 239°C, compared to the behavior for the unmodified resin. When using 10 wt % of PMS, the  $\alpha'$ -relaxation peak shifted to 247°C. The

$\alpha'$ -relaxation peak became large with increasing PMS concentration. The appearance of the new  $\alpha'$ -relaxation peak in the  $\tan\delta$  curve indicates the existence of the phase-separated structure for the PMS-modified resin. The storage moduli at room temperature for the modified resins were slightly smaller than the value for the unmodified resin.

Figure 7 shows the PMS  $MW$  dependence of dynamic viscoelastic behaviors of the modified resin on 10 wt % inclusion. When using low  $M_w$  (85,000) PMS, the  $\alpha$ -relaxation peak position shifted slightly toward higher temperature compared to that for the unmodified resin. The  $\alpha$ -relaxation peak position of the modified resins approached that of the unmodified resin with increasing PMS  $MW$ . The  $\alpha'$ -relaxation peak position hardly changed except for the lowest  $M_w$  (85,000) PMS. The storage moduli at room temperature for the modified resin were comparable or slightly smaller than the value for the unmodified resin.



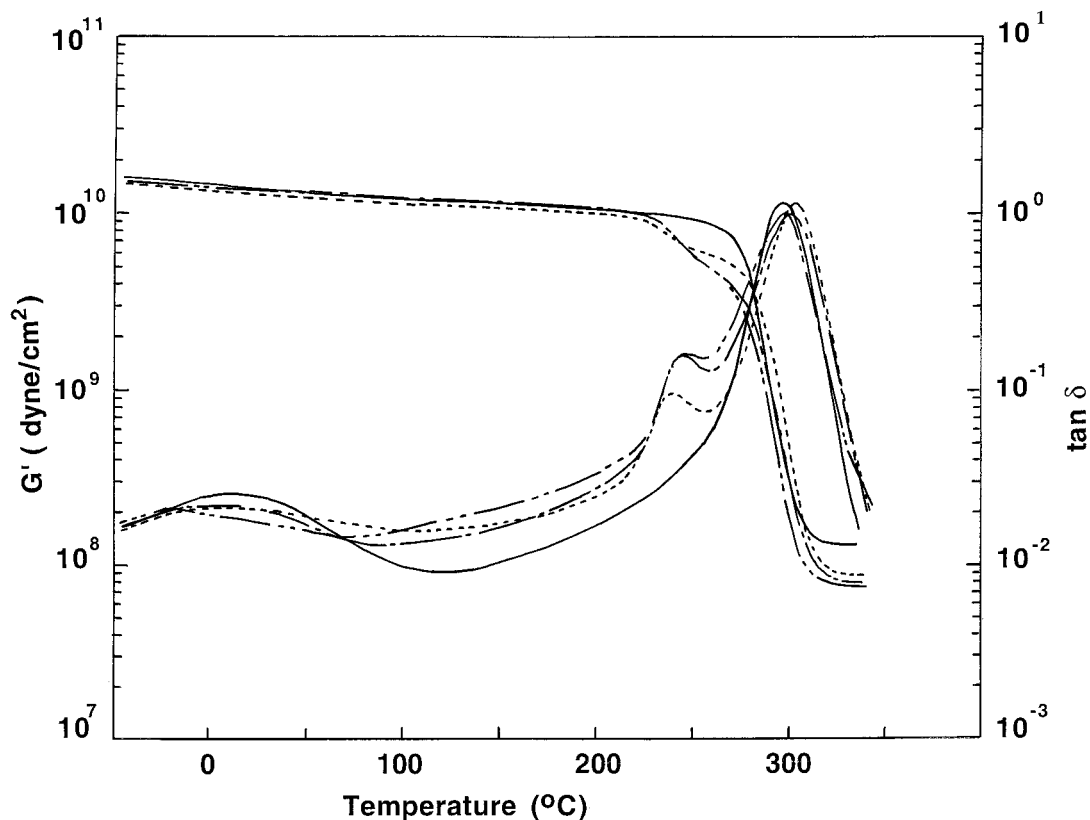
**Figure 6** Dynamic viscoelastic analysis of unmodified and PMS-modified resins: dependence on PMS content. PMS ( $M_w$  133,000); (—) 0 wt % (control); (- - -) 7.5 wt % addition; (- · -) 10 wt % addition.

## DISCUSSION

PMS was soluble in the cyanate ester resin without solvents and effective as the modifier for the cyanate ester resin. The morphologies of the modified resins changed from the particulate structure to cocontinuous or phase-inverted structures, depending on PMS  $M_w$  and concentration. The fracture behavior corresponds to the morphologies of the modified resins as follows.

When using 10 wt % of PMS ( $M_w$  85,000),  $K_{IC}$  for the modified resin increased 115% and the morphology of the modified resin was intermediate structure between particulate and cocontinuous phase structures [Fig. 5(a)]. PMS having  $M_w$  133,000 was the most effective modifier and its 10 wt % inclusion led to a 160% increase in  $K_{IC}$  because of the cocontinuous phase structure of the modified resin [Fig. 4(c)], whereas  $K_{IC}$  increased by only 35% on lower concentration (7.5 wt %) of the same modifier and the modified resin had the particulate structure with PMS-rich particles [Fig. 4(a)]. PMS ( $M_w$  ca. 130,000) were ef-

fective in the inclusion range of 9–12 wt % and the modified resins had the cocontinuous phase structure. When using 15 wt % of PMS ( $M_w$  133,000), the morphology of the modified resin became the phase-inverted structure [Fig. 4(e)], and the  $K_{IC}$  value and mechanical properties were deteriorated abruptly. Toughening could be achieved because of the absorption of fracture energy due to the ductile drawing and tearing of the PMS-rich continuous phase in the present modification as well as in the modification of epoxy<sup>25</sup> and bismaleimide<sup>26</sup> resins with PMS, whereas the phase-inverted morphology was undesirable: toughening was attained because of the phase-inverted structure in the modification of epoxies with poly(ether imide)<sup>7</sup> or polysulfone having pendant amino groups.<sup>6</sup> The relationship between the fracture enhancement behavior and the extent of dispersion of the cocontinuous phases is interesting. In the modification with PMS having  $M_w$  133,000 or 189,000, the cured resins had cocontinuous phase structure and the extent of dispersion of the cocontinuous phase



**Figure 7** Dynamic viscoelastic analysis of unmodified and PMS-modified resins: dependence on PMS molecular weight. PMS 10 wt % addition; (—) control; (---) PMS  $M_w$  85,000; (- - -) PMS  $M_w$  189,000; (— — —) PMS  $M_w$  332,000.

became higher with increasing PMS  $MW$  [Fig. 5(b–d)], whereas  $K_{IC}$  for the modified resins decreased inversely (Fig. 2). This indicates that there is an optimum extent of dispersion of the cocontinuous phase to improve the brittleness of the cured cyanate ester resin. Such a relation between enhancement in the fracture toughness and the morphology of the modified resin was also observed in the modification of epoxy<sup>25</sup> and bis-maleimide<sup>27</sup> resins with PMS. The PMS-rich phases in the modified resins were removed by etching [Fig. 4(f)]. This indicates that there is no chemical interfacial adhesion between the cyanate ester matrix and PMS. A decrease in flexural strength could be explained by insufficient interfacial adhesion, based on physical interactions such as van der Waals forces.

## CONCLUSIONS

PMS was the effective modifier for the cyanate ester resin. The morphology of the modified resin

changed from the particulate structure to cocontinuous phase or phase-inverted structures, depending on PMS  $MW$  and concentration. Toughening was achieved because of the cocontinuous phase structure. The extent of dispersion of the cocontinuous phase became higher with increasing PMS  $MW$  and  $K_{IC}$  for the modified resins decreased inversely. Inclusion of 10 wt % PMS ( $M_w$  133,000) led to 160% increase in  $K_{IC}$  with retention in flexural modulus and  $T_g$ , and a loss of flexural strength, compared to the values of the unmodified cured cyanate ester resin. Water absorptivity of the modified resin was comparable to the unmodified resin.

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