

# Modification of Bismaleimide Resin with *N*-Phenylmaleimide-Styrene-*p*-Hydroxystyrene and *N*-Phenylmaleimide-Styrene-*p*-Allyloxystyrene Terpolymers

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**ABSTRACT:** *N*-Phenylmaleimide-styrene-*p*-hydroxystyrene terpolymers (PMSH) and *N*-phenylmaleimide-styrene-*p*-allyloxystyrene terpolymers (PMSA), containing pendant functionalities, were prepared and used to improve the toughness of the bismaleimide resin composed of *bis*(4-maleimidediphenyl)methane and *o,o'*-diallyl bisphenol A. PMSH (0.5 mol % *p*-hydroxystyrene [HSt] unit) was more effective as a modifier than PMSA (0.5 mol % *p*-allyloxystyrene unit). When using 5 wt % of PMSH with 0.5 mol % HSt unit, the fracture toughness ( $K_{IC}$ ) for the modified resin increased 60% with only a modest loss of flexural strength and with retention in flexural modulus and the glass transition temperature. Morphologies of the modified resins changed from particulate to cocontinuous and to inverted phase structures, depending on the modifier structure and content. The most effective improvement of properties for the modified resins could be attained because of the cocontinuous structure. The toughening mechanism was discussed in terms of the morphological characteristics of the modified bismaleimide resin systems. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 1451–1461, 1997

**Key words:** bismaleimide resin; modification; *N*-phenylmaleimide-styrene-*p*-hydroxystyrene terpolymers; *n*-phenylmaleimide-styrene-*p*-allyloxystyrene terpolymers; fracture toughness

## INTRODUCTION

Addition polyimide resins are some of 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 are also attractive because of good processability and nonvolatility. Recently, a two-component bismaleimide system (Matrimid 5292), composed of *bis*(4-maleimidediphenyl)methane (BMI) and

*o,o'*-diallyl bisphenol A (DBA), has been developed by Ciba Geigy to improve mechanical properties and processability.<sup>1</sup> However, the fracture toughness of the two-component bismaleimide is not yet sufficient for use as a composite matrix.

The toughness of epoxy resins has been increased by blending with reactive liquid rubbers such as carboxyl-terminated butadiene acrylonitrile rubbers<sup>2</sup> or epoxide-containing acrylic elastomers.<sup>3–7</sup> Engineering thermoplastics are interesting materials as modifiers for bismaleimide resins from the viewpoint of the retention of mechanical and thermal properties. Engineering thermoplastics examined as modifiers for epoxies include poly(ether sulfone),<sup>8–10</sup> polysulfone,<sup>11–13</sup> poly(etherimide),<sup>14–17</sup> poly(ether ketone),<sup>18–20</sup> poly-

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(phenylene oxide),<sup>21–23</sup> poly(butylene terephthalate),<sup>24–26</sup> and soluble aromatic polyesters.<sup>27–29</sup>

Modification of the bismaleimide resin has been carried out on the basis of information on the toughening of epoxies in our laboratory. In our previous articles, we have reported that *N*-phenylmaleimide-styrene copolymers (PMS) were effective modifiers for both the bismaleimide and the epoxy resins.<sup>30–32</sup> *N*-Phenylmaleimide-styrene-*p*-hydroxystyrene terpolymers (PMSH) having functionalities and hybrid modifiers composed of PMS and PMSH were also effective modifiers for epoxies.<sup>33,34</sup>

This article reports the modification of the two-component bismaleimide resin with both PMSH and *N*-phenylmaleimide-styrene-*p*-allyloxystyrene terpolymers (PMSA) containing functional groups that react with the maleimide group. The effects of chemical structure, molecular weight, and amount of the modifiers used on the toughness of the cured resin were examined.

## EXPERIMENTAL

### Materials

The bismaleimide resin was a commercial product composed of BMI and DBA (Matrimid 5292). *N*-Phenylmaleimide (PMI) was provided by Nippon Shokubai Co. and used as received. *p*-*tert*-Butoxystyrene (tBSt) was supplied by Hokko Chemical Industrial Corporation. Styrene (St) and tBSt were purified in the usual ways. Other reagents were used as received.

### Measurements

<sup>1</sup>H-nuclear magnetic resonance (NMR) spectra of the terpolymers were recorded on a 90-MHz instrument (JEOL JNM-9MX 90) at 60°C using dimethyl sulfoxide-*d*<sub>6</sub> as solvent and tetramethylsilane as internal standard. Molecular weights of the terpolymers were measured by gel permeation chromatography (Shimadzu LC-5A instrument) with 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 bend geometry at a crosshead speed of 1 mm/min (ASTM E-399). The glass transition temperatures ( $T_g$ ) of both terpolymers and cured resins were measured as the onset temperatures

by differential scanning calorimetry (Shimadzu DSC 41M type) at a heating speed of 10°C/min in an atmosphere of nitrogen. Scanning electron micrographs (SEM) were taken with a Hitachi SEM-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 350°C at a heating rate of 5°C/min at a frequency of 1 Hz (dynamic mode, 0.1% strain) under nitrogen.

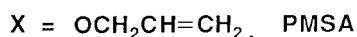
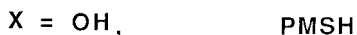
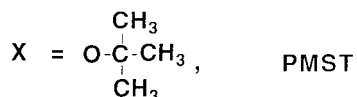
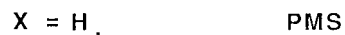
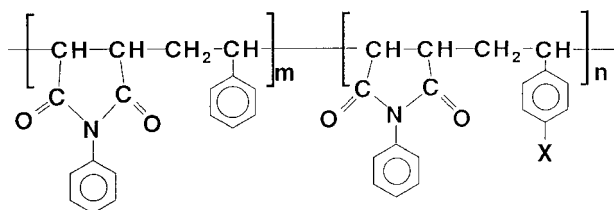
### Preparation of Modifiers

*N*-Phenylmaleimide-styrene-*p*-*tert*-butoxystyrene terpolymers (PMST) were prepared by radical polymerization, as reported previously.<sup>33</sup> PMSH was prepared by de-*tert*-butylation of PMST. PMSA was prepared by the reaction of allyl bromide and *p*-hydroxystyrene (HSt) unit in PMSA with a phase transfer catalyst, tetrabutylammonium bromide (TBAB). A typical procedure was as follows.

A flask was charged with 60 g of PMSH (5 mol % HSt unit, GPC-average molecular weight ( $M_{GPC}$ ) 359,000) and 900 mL of dichloromethane. After the PMSH was dissolved, 25.9 g (0.214 mol) of allyl bromide, 3.4 g of sodium hydroxide, 600 mL of water, and 13.8 g of TBAB were added. The mixtures were stirred vigorously at room temperature for 24 h. The polymer dichloromethane solution was poured into methanol and washed with methanol, and the polymer isolated was dried *in vacuo* at 60°C. The crude dry polymer was purified by reprecipitation with THF/hexane and dried *in vacuo* at 60°C. The yield was 94%.  $M_{GPC}$  was 386,000. The *p*-allyloxystyrene unit in PMSA was 4.9 mol % by <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 60°C).

### Curing Procedure

The terpolymers were dissolved in DBA by heating at 160°C. Then, BMI was added to the mixture, which was kept at 130°C to dissolve BMI. DBA and BMI were used in a molar ratio of 1 : 1. The resulting clean mixture was poured into a mold preheated at 130°C and degassed *in vacuo* to obtain 4- or 7-mm-thick plaques. The mold consisted of one pair of upright and metal clip-held glass plates spaced by a U-shaped silicon rubber stick. The resin plate obtained was machined by a diamond saw. The amount (wt %) of the modifiers was calculated based on the Matrimid 9252 system. The curing cycle was 160°C/3 h + 180°C/1 h + 200°C/2 h



Scheme 1

+ 250°C/6 h. After curing, the oven temperature was decreased to 100°C at 0.5°C/min.

## RESULTS AND DISCUSSION

### Characterization of the Terpolymers

PMST was prepared in a quantitative yield. The molecular weights of PMST could be con-

trolled with dodecanethiol as a transfer agent. The terpolymer compositions were equal to the feed compositions by <sup>1</sup>H NMR spectroscopy. It is well known that the radical copolymerization of PMI and St gives alternating copolymers.<sup>35</sup> The terpolymerization of PMI, St, and tBSt must also afford alternating copolymers composed of both PMI-St and PMI-tBSt units. PMSH was prepared by de-*tert*-butylation of PMST (Scheme 1). PMSA was prepared by the allylation of PMSH with allyl bromide. The polydispersity of PMSA became large. Then, the GPC-average molecular weight ( $M_{GPC}$ ) was used as a measure of the molecular weight (MW) of the terpolymers, and the MW dependence of physical properties for the modified resins was discussed by using  $M_{GPC}$  in this study. Table I reports some characteristic properties of the terpolymers. In spite of the carbon-carbon single bond repeating units, PMSH and PMSA have high  $T_g$  values of ca. 220°C, as well as PMS, because the bulkiness of two side groups prevents the molecular motion of the main chain. Furthermore, hydrogen bonding also contributed to the increase in  $T_g$ , based on the *p*-hydroxyphenyl units in PMSH, as reported previously.<sup>33,36</sup>

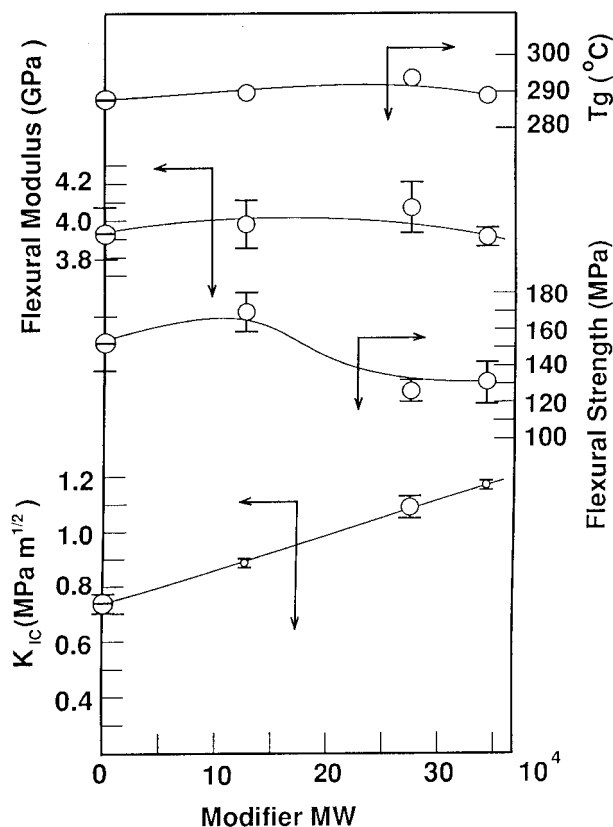
Table I Characterization of the Copolymers

Entry No.	Copolymer Composition <sup>a</sup>			$M_{GPC}^b$ (10 <sup>4</sup> )	$M_w^b$ (10 <sup>4</sup> )	$M_n^b$ (10 <sup>4</sup> )	$M_w/M_n$	$T_g^c$ (°C)
	PMI	St	HSt (ASt)					
PMS	50	50	0	24.7	29.3	10.7	2.7	225
PMSH series: PMSH								
15	50	49.5	0.5	12.6	12.7	4.7	2.7	229
12	50	49.5	0.5	27.4	23.2	8.4	2.8	229
14	50	49.5	0.5	34.2	27.6	8.7	3.2	230
11	50	49	1	34.5	40.0	14.1	2.8	225
10	50	47.5	2.5	36.5	30.1	12.9	2.7	228
13	50	45	5	32.8	25.5	9.1	2.8	233
7	50	35	15	23.2	30.0	8.5	3.2	239
PMSA series: PMSA								
9	50	49.5	(0.5)	37.3	37.6	10.6	3.5	225
8	50	49	(1)	33.8	42.4	9.1	4.7	226
10	50	47.5	(2.5)	42.7	832	12.4	67.1	227
4	50	45	(5)	20.4	337	9.1	36.8	220
6	50	40	(10)	22.9	35.9	7.4	4.8	218

<sup>a</sup> mol %.

<sup>b</sup> By GPC.

<sup>c</sup> By differential scanning calorimetry.



**Figure 1** Dependence of physical properties for the modified resins on PMSH MW. PMSH (0.5 mol % HSt unit), 5 wt % addition. (○) Control.

### Mechanical and Thermal Properties of Modified Resins

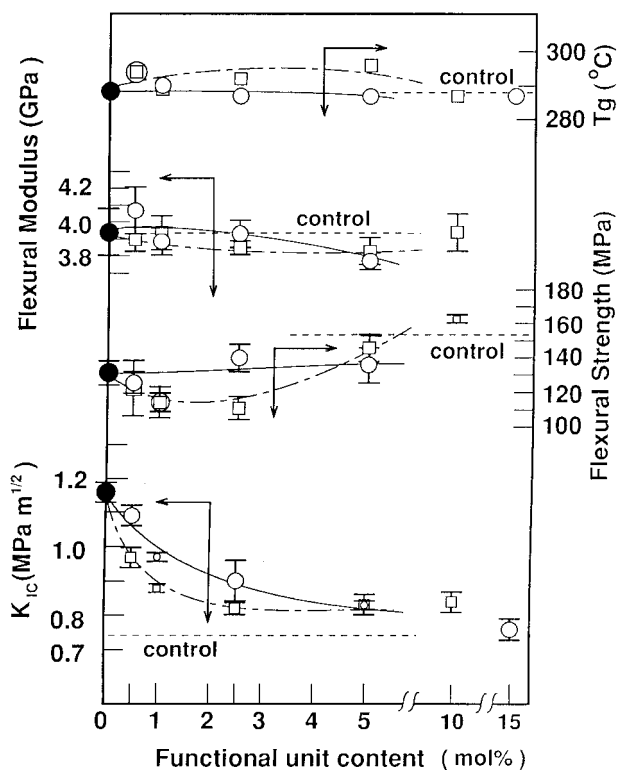
The cured parent bismaleimide resin was transparent, as reported previously.<sup>30</sup> The transparency of the modified resins depended on the terpolymer structure. The cured resins modified with the terpolymers containing less than 2.5 mol % functional units (HSt or *p*-allyloxystyrene (ASt) units) became translucent during curing. When using 5 wt % of PMSH (5 mol % HSt unit) or PMSA (5 mol % ASt unit), the modified resins were transparent. The results indicate that compatibility of the terpolymer with the bismaleimide matrix increased with increasing functional unit content because of reactive blends.

Figure 1 shows the modifier MW dependence of the mechanical and thermal properties for the modified bismaleimide resins on 5 wt % of PMSH (0.5 mol % HSt unit). The fracture toughness,  $K_{IC}$ , for the modified resins increased linearly with increasing PMSH MW: the  $K_{IC}$  for the PMS-modified resins increased discontinuously with an increase in PMS MW, as reported previously.<sup>30</sup>

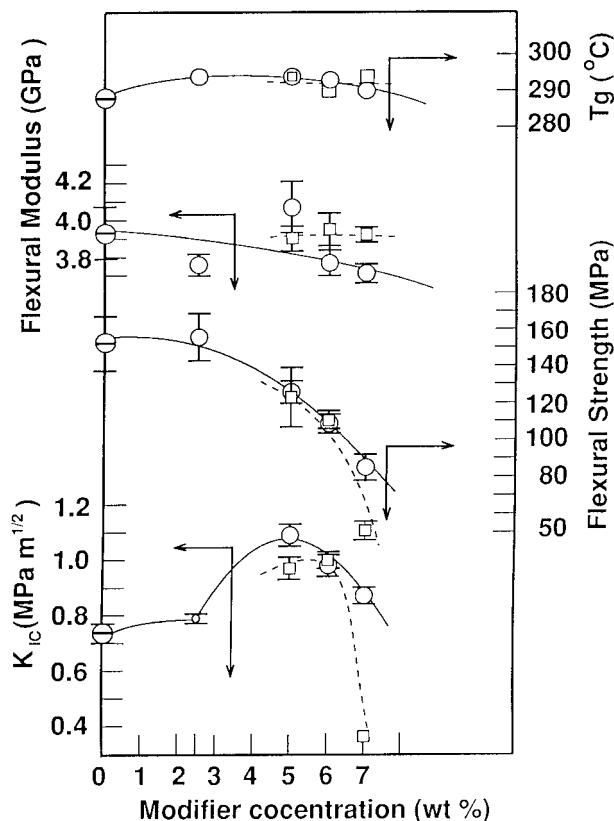
The use of higher MW PMSH led to a decrease in flexural strength. Flexural modulus and  $T_g$  were equal to or higher than those for the unmodified bismaleimide resin.

Figure 2 shows the dependence of the mechanical and thermal properties for the modified resins on the terpolymer structure. PMSH was more effective as a modifier than PMSA. The  $K_{IC}$  for the modified resins decreased with increasing functional unit content in the terpolymers, when the  $K_{IC}$  for the PMSA-modified resins decreased more abruptly than that for the PMSH-modified materials. The fracture behavior in the bismaleimide/PMSH modification is different from that in the modification of the aromatic diamine-cured epoxy resin with PMSH: in the modification of epoxies with PMSH, the abrupt decrease in  $K_{IC}$  was not observed and the modified resins had balanced properties with a 10 wt % addition of PMSH (less than 3 mol % HSt unit).<sup>33</sup> Flexural strength for the modified resins increased gradually, and flexural moduli and  $T_g$  hardly changed with increasing functional unit content, compared with those for the unmodified resin.

Figure 3 shows the mechanical and thermal



**Figure 2** Dependence of physical properties for the modified resins on the modifier structure with 5 wt % of the modifier. (●) PMS, (○) PMSH, (□) PMSA.



**Figure 3** Physical properties of the modified resins as a function of modifier concentration. (⊖) Control, (○) PMSH (0.5 mol % HSt unit; MW 274,000), (□) PMSA (0.5 mol % ASt unit, MW 373,000).

properties of the modified resins as a function of the concentration of the modifiers. The  $K_{IC}$  values for the PMSH (0.5 mol % HSt unit)-modified resins increased discontinuously with a 5 wt % addition of PMSH and then decreased. PMSA (0.5 mol % ASt unit) was effective with a 5–6 wt % addition to toughen the bismaleimide resin, but the  $K_{IC}$  decreased abruptly with a 7 wt % addition. The fracture behavior corresponds to the morphology of the modified resin, as shown below. Flexural strength decreased with increasing modifier content. Flexural moduli for the modified resins were comparable to that for the parent bismaleimide resin. The  $T_g$  values for the modified resins were equal or slightly high, compared with that for the parent resin.

In general, an advantage of reactive modifiers over nonreactive materials is that they produce higher solvent resistance in the modified resins. In the modification of epoxies with PMS, the PMS-rich phases were etched out clearly by THF in both particulate and cocontinuous phase struc-

tures.<sup>31</sup> However, in the epoxy/PMSH modification system, the PMSH-rich phases could not be removed by THF etching, when the modified resins had particulate or cocontinuous morphologies. In the modification of the bismaleimide resin with PMS, the modified resins exhibited excellent solvent resistance and could not be etched out at all by THF or  $\text{CHCl}_3$  (at room temperature for 3 days). This would be because of the high physical interfacial adhesion between the matrix and the modifiers based on their structural similarity, where the polar imide units in the matrix and the modifiers would play an important role. The PMSH- or PMSA-modified resins also exhibited high solvent resistance.

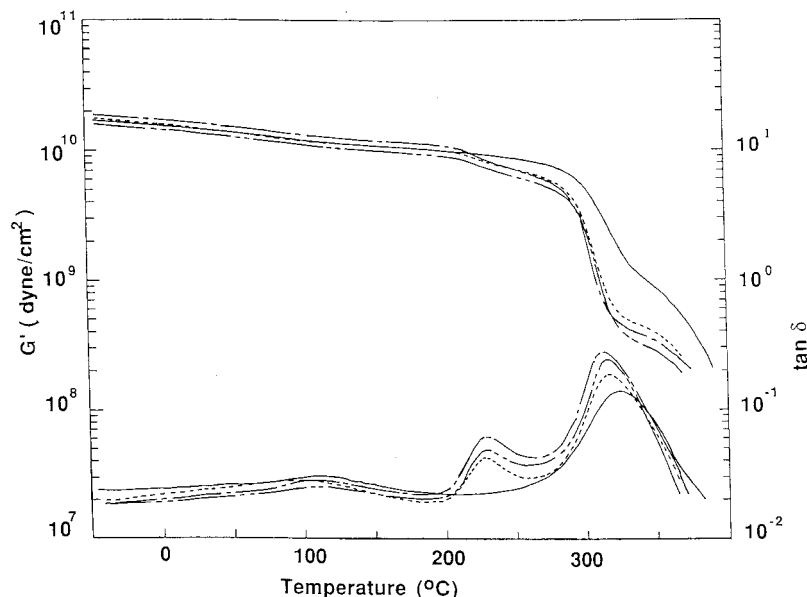
### Dynamic Viscoelastic Analysis of the Modified Resins

Dynamic viscoelastic analysis can give information on the microstructure of cured resins. Figure 4 shows the storage moduli,  $G'$ , and  $\tan \delta$  curves for the unmodified and modified resins. In the modification with 5 wt % of the modifiers, the peak positions of the  $\alpha$ -relaxation in the  $\tan \delta$  curve shifted slightly toward lower temperature and their magnitude became larger compared with the dynamic viscoelastic behavior for the parent bismaleimide resin. New relaxation ( $\alpha'$ -relaxation) peaks were observed at ca. 230°C, which would be based on the modifier-rich phase. The peak position and the magnitude of the  $\alpha'$ -relaxation hardly changed, independent of the modifier structure. The appearance of the  $\alpha'$ -relaxation peak indicates the presence of the phase-separated structure for the modified resins. Storage moduli at room temperature were comparable to that for the unmodified resin.

### Morphologies of the Modified Resins

The morphologies of the modified resins were investigated by scanning electron microscopy. The parent bismaleimide resin had only one phase, as reported previously.<sup>30</sup> Inclusion of the modifiers led to two phase morphologies. Morphologies of the modified resins depended on the structure and concentration of the modifiers.

Figure 5 contains SEMs of the fracture surfaces for the cured resins modified with 5 wt % of PMSH (0.5 mol % HSt unit). The morphologies of the modified resins changed drastically depending on PMSH MW. When using 5 wt % of PMSH (0.5 mol % HSt unit, MW 126,000), the modified resin



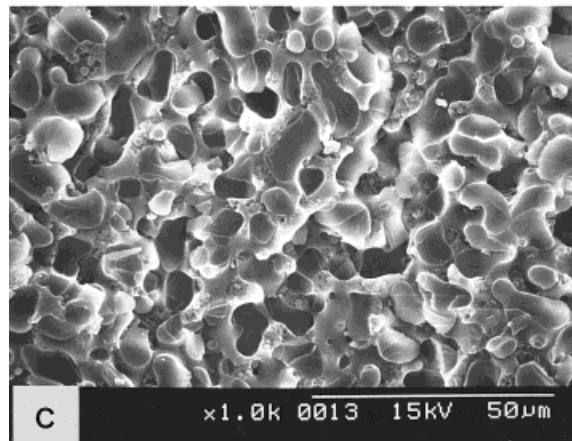
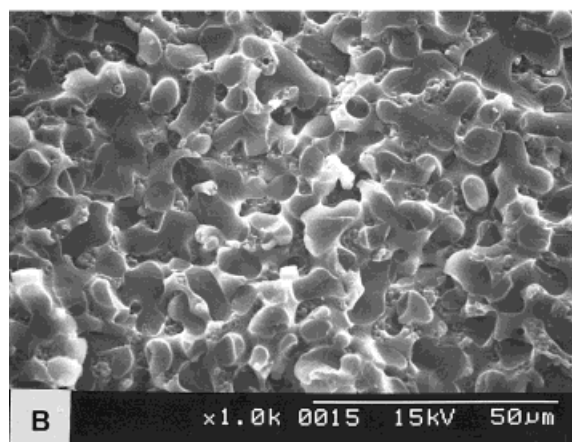
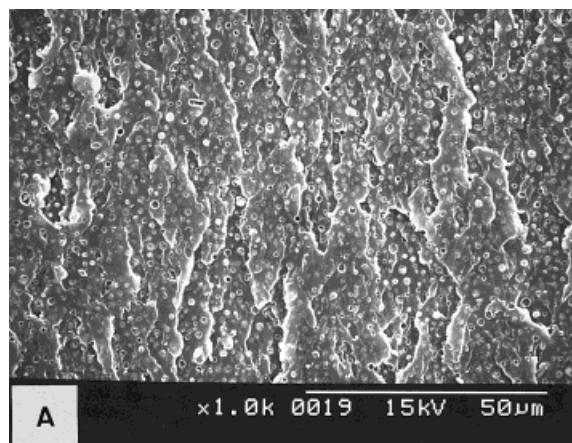
**Figure 4** The dependence of dynamic viscoelastic behavior of unmodified and modified resins. (—) 0 wt % (control); (---) PMS (MW 274,000), 5 wt % addition; (.....) PMSH (0.5 mol % HSt unit, MW 247,000), 5 wt % addition; (- - -) PMSA (0.5 mol % ASt unit, MW 373,000), 5 wt % addition.

had a particulate structure having PMSH-rich particles dispersed in the bismaleimide matrix [Fig. 5(A)]. The PMSH (MW 274,000)-modified resin had a cocontinuous phase morphology as well as the PMSH (MW 342,000)-modified material, and the extents of dispersion of the PMSH-rich phase were similar to each other [Fig. 5(B) and (C)].

Figures 5(B) and 6 show the dependence of the morphology of the modified resins on the modifier structure with a 5 wt % PMSH addition. The PMSH (0.5 mol % HSt unit)-modified resins have a cocontinuous phase morphology similar to that of the cured resin modified with PMS having no functional group [Figs. 6(A) and 5(B)]. The extent of dispersion of the PMSH-rich phase became higher by blending PMSH containing the 1.0 mol % HSt unit [Fig. 6(B)]. In the modification with PMSH containing the 5 mol % HSt unit (MW 328,000), the cured resin became transparent and its morphology was ill defined, even at a higher magnification ( $\times 3,000$ ) [Fig. 6(C)]. The morphological results also indicate that the compatibility of PMSH with the bismaleimide matrix increased with increasing HSt unit content in the modifier. The morphological results correspond to the fracture behavior for the modified resins: the  $K_{IC}$  for the modified resin increased because of the cocontinuous phase morphology (see Fig. 2).

Increasing PMSH (0.5 mol % HSt unit) concentration also led to a change in the morphology of the modified resin [Figs. 5(B) and 7]. With 2.5 wt % of PMSH (0.5 mol % HSt unit), the modified resin had a particulate morphology [Fig. 7(A)]. When using 5 wt % of the same modifier, the morphology of the modified resin became cocontinuous phase structures [Fig. 5(B)], where  $K_{IC}$  increased discontinuously (Fig. 3). The extent of dispersion of the cocontinuous phase became higher by blending 7 wt % of the same modifier [Fig. 7(B)], and the  $K_{IC}$  decreased compared with that for the 5 wt %-modified resin. The relationship between the improvement in toughness and the morphology of the modified resin corresponds to the previous modification results in the modification of both the bismaleimide resin with PMS<sup>30</sup> and the epoxy resin with PMS or PMSH.<sup>31-33</sup>

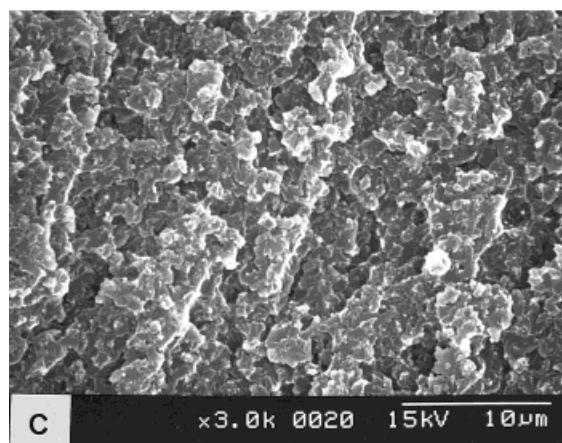
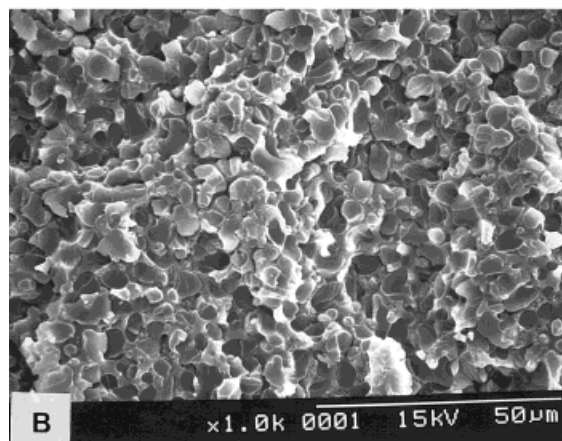
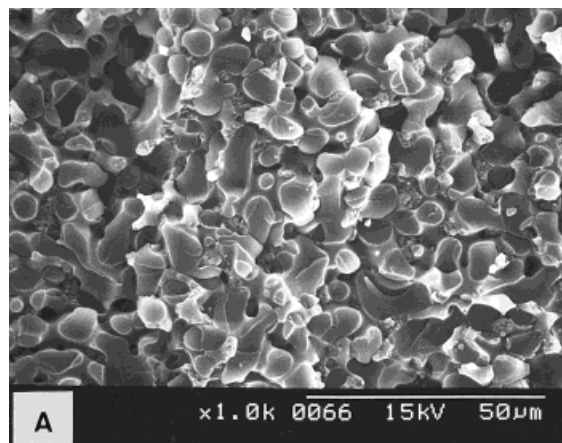
Figure 8 shows SEMs of the fracture surfaces for the PMSA-modified resins. The contours of a cocontinuous phase structure were rather obscure with the 5 wt % of PMSA with the 0.5 mol % ASt unit [Fig. 8(A)], compared with the morphology of the cured resin modified with PMSH, having similar MW and functional unit content [Fig. 5(B)]. This indicates that the ASt unit is more effective in improving the interfacial adhesion between the two incompatible phases than the HSt unit. The extent of dispersity of the PMSA-rich



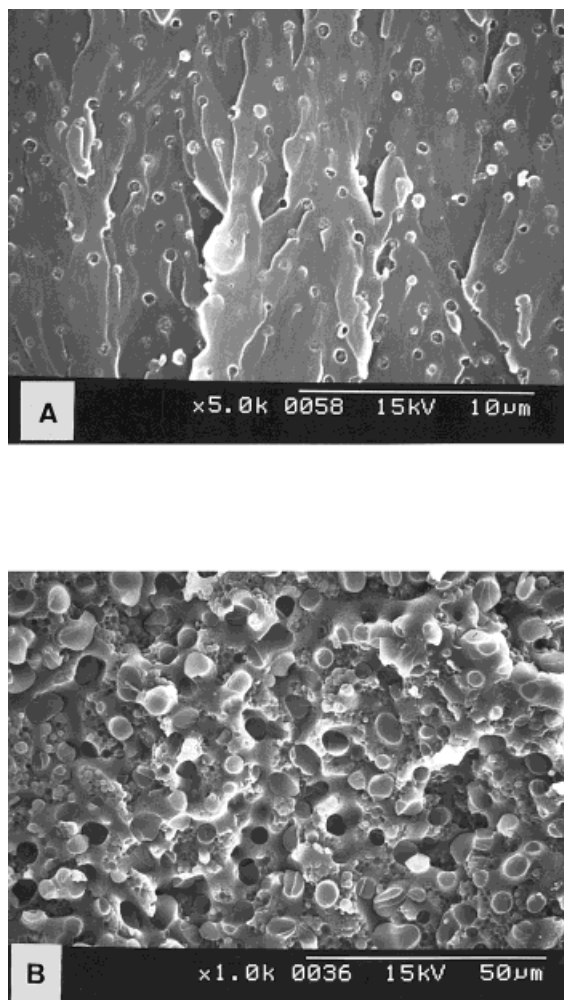
**Figure 5** SEMs of fracture surfaces for the cured resins modified with 5 wt % of PMSH (0.5 mol % HSt unit). MW of PMSH used: (A) 126,000, (B) 274,000, (C) 342,000.

phase became higher with increasing ASt unit content in PMSA [Fig. 8(B)]. The modified resin became transparent by blending 5 wt % of PMSA having the 10 mol % ASt unit, and the phase-separated structure disappeared [Fig. 8(C)]. It is

noteworthy that the modified resin had a typical phase-inverted structure when using 7 wt % of PMSA (ASt unit, 0.5 mol %; MW 373,000) [Fig. 8(D)] and that the phase-inverted structure in



**Figure 6** SEMs of fracture surfaces for the cured resins modified with 5 wt % of the modifiers. (A) PMS (MW 247,000), (B) PMSH (1.0 mol % HSt unit, MW 345,000), (C) PMSH (5.0 mol % HSt unit, MW 328,000).



**Figure 7** SEMs of fracture surfaces for the cured resins modified with PMSH (0.5 mol % HSt unit, MW 274,000). (A) 2.5 wt % addition, (B) 7 wt % addition.

the present modification is unsuitable in improving the toughness as well as in the modification of the bismaleimide resin with PMS.<sup>30</sup>

The difference in these morphological behaviors between PMS/bismaleimide and reactive modifiers [PMSH or PMSA]/bismaleimide curing systems cannot be explained by the solubility parameter; the SP values [ $(\text{MJ}/\text{m}^3)^{1/2}$ ] for the Matrimid A/B, PMS, PMSH (5 mol % HSt unit), and PMSA (5 mol % ASt unit) are 27.66, 26.99, 27.13, and 26.87, respectively (values calculated by the method of Fedors<sup>37</sup>).

### Discussion on the Toughening Mechanism

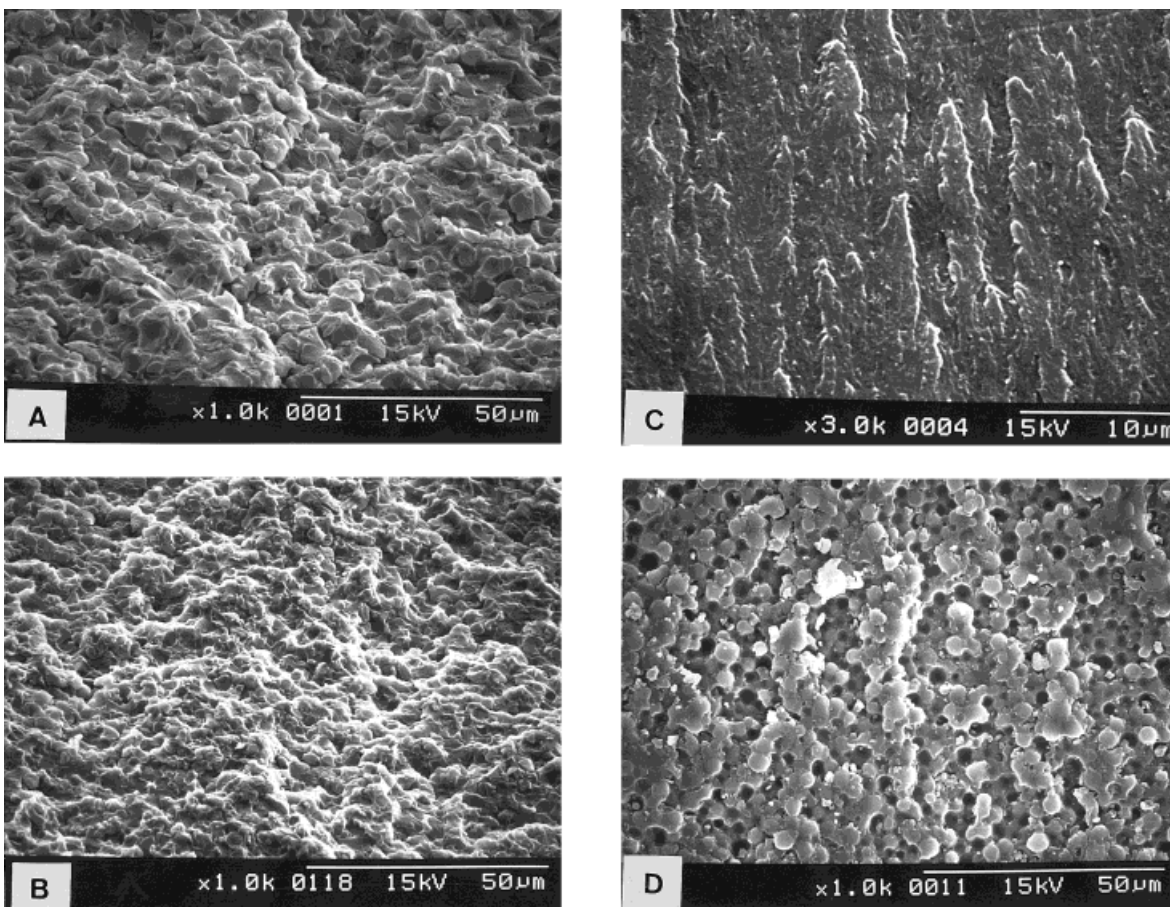
The morphological behavior of the modified resin is interesting, and it is instructive to consider the

toughening mechanism. The morphologies of the modified resins depend on the curing conditions as phase separation competes with gelation or vitrification. In the modification of lightly cross-linked epoxies with reactive liquid rubbers, the modified resins had particulate structures and toughening can be achieved by the formation of a shear band of the matrix near the crack based on the deformation of the dispersed particles as stress concentrators.<sup>2</sup> In the modification of highly crosslinked epoxy and bismaleimide matrices, the extent of shear band formation by deformed particles becomes lower and the particulate morphology is rather unsuitable for improving toughness.

In the modification of epoxies with thermoplastics such as poly(ether sulfone), the modified resins have particulate, cocontinuous, or phase-separated morphologies, depending on both the resin compositions and the curing conditions.<sup>38</sup> Toughening of epoxies by thermoplastics could be achieved because of cocontinuous or phase-inverted structures: the fracture energy could be absorbed by ductile drawing and tearing of the modifier-rich phase. Furthermore, the good interfacial adhesion between the matrix and the modifier is important to improve the toughness of the resin, as shown in the modification of epoxies with rubber<sup>2,3</sup> or engineering thermoplastics.<sup>11–13,20</sup> We have also reported that the hybrid modifiers composed of PMS and PMSH were effective in improving the interfacial adhesion between the epoxy matrix and the modifier, which was ascertained by SEM observation, and that the modified resins had balanced physical properties.<sup>34</sup>

PMS was effective as the modifier for improving the toughness of both the bismaleimide<sup>30</sup> and the epoxy resins,<sup>31,32</sup> and the toughening could be attained based on the cocontinuous phase structure in both modification systems, where the fracture energy was absorbed due to ductile drawing and tearing of the PMS-rich continuous phase. In the modification of bismaleimides with PMS, the inclusion of 5 wt % of PMS with the weight-average MW 231,000 led to a significant increase in  $K_{IC}$  together with the moderate decrease in the flexural strength. Furthermore, the effect of the matrix composition on the toughening of the cured resins was examined in the modification of the bismaleimide resin with PMS, where the matrix compositions were controlled by using DBA and triallyl isocyanurate (TAIC).<sup>39</sup> The increase in TAIC content resulted in the lower extent of dispersion of the PMS-rich phase, but  $K_{IC}$  for the





**Figure 8** SEMs of fracture surfaces for the cured resins modified with PMSA. (A) PMSA (0.5 mol % ASt unit, MW 373,000), 5 wt % addition; (B) PMSA (1.0 mol % ASt unit, MW 338,000), 5 wt % addition; (C) PMSA (10.0 mol % ASt unit, MW 229,000), 5 wt % addition; (D) PMSA (0.5 mol % ASt unit, MW 373,000), 7 wt % addition.

modified resin increased up to a 20 eq % addition of TAIC and then decreased. The results indicate that there is an optimal extent of dispersion of the cocontinuous phase to improve the toughness of the bismaleimide resins to a greater extent.

In the modification of epoxies with PMS and the related nonreactive modifiers, the moderate decrease in flexural strength would be caused by poor interfacial adhesion between the matrix-rich and the PMS-rich phases. To obtain more effective modifiers, PMSH having functionalities was prepared and examined as the modifier for epoxies.<sup>33</sup> Compatibility of PMSH with the epoxy matrix increased with increasing HSt unit content. When using 10 wt % PMSH having less than 5 mol % HSt units, the modified resin had cocontinuous phase morphologies. The extent of dispersion of the cocontinuous phase became gradually higher with increasing up to 3 mol % HSt unit content, and the dispersity became abruptly higher by

blending PMSH having a 4 mol % HSt unit. PMSHs having less than 3 mol % HSt units were effective modifiers for toughening, and the modified resins had balanced physical properties. PMSHs having more than 4 mol % HSt units were less effective. The results also indicate that there is an optimal extent of dispersion of the cocontinuous phase in reducing the brittleness of epoxies by modification with PMS and the related modifiers as well as in the modification of bismaleimides with PMS.

In this study, the terpolymers having a smaller functional unit content were prepared and used as modifiers for the bismaleimide resin, considering the modification results in the modification of epoxies with PMSH.<sup>33</sup> When using PMSH with a 0.5 mol % HSt unit, the modified resins had the cocontinuous phase morphology and the extent of dispersion of the cocontinuous phase was similar to that for the PMS-modified resin [Fig. 5(B) and

6(A)]; this would not be an optimal extent of dispersion, because the extent of dispersion of the cocontinuous phase in the PMS/Matrimid system [Fig. 6(A)] is higher and undesirable to improve the toughness of the bismaleimide resin, compared with that in the PMS/Matrimid/TAIC system, as reported previously.<sup>39</sup> The PMSH (1 mol % HSt unit)-modified resin also had the cocontinuous phase morphology, but the dispersity of the cocontinuous phase became higher because of the increase in the compatibility of PMSH with the epoxy matrix [Fig. 6(B)]. With 5 wt % of PMSH (5 mol % HSt unit), the contours of the continuous phases were ill defined, even at the higher magnification [Fig. 6(C)].  $K_{IC}$  for the modified resin decreased with the increase in the extent of dispersion of the cocontinuous phases. A tendency to increase in compatibility with increasing functional group content was significant in the PMSA modification, compared with the PMSH modification system. When using PMSA with a 0.5 mol % ASt unit, the morphology of the modified resin was quite different from that of the PMS-modified resin [Fig. 6(A) and 8(A)] and the contours of the continuous phases were obscure. Its tendency became significant with increasing ASt unit content [Fig. 8(B) and (C)]. The increase in the dispersity also corresponds to the decrease in  $K_{IC}$  in the modification with PMSA. Considering the modification results (Fig. 2) and morphological behavior [Fig. 5(C), 6(B), and 8(A) and (B)], PMSA reacts with the matrix faster than PMSH and the extent of dispersion of the modifier-rich phase in the PMSA-modified resin is higher than that of the PMSH-modified resin; therefore, PMSA is less effective as the modifier than PMSH. The increase in the interfacial adhesion is favorable for toughening, and the higher extent of dispersity of the cocontinuous phase is unfavorable. These adverse effects would also act in the present modification systems as reported in the modification of bismaleimides and epoxies with PMS and the related modifiers.<sup>30-33</sup>

## CONCLUSIONS

PMSH and PMSA having functional groups were prepared and used to improve the interfacial adhesion between the modifier and the matrix. PMSH was the effective modifier for improving the toughness of the bismaleimide resin as well as PMS. PMSA was less effective than PMSH. The most effective modification for the modified

resins could be attained because of the cocontinuous structures of the modified resins in both modification systems. When using 5 wt % of PMSH having a 0.5 mol % HSt unit,  $K_{IC}$  for the modified resin increased 60% with a medium loss of flexural strength and with retention in flexural modulus and  $T_g$ . The extent of dispersion of the modifier-rich continuous phases became high, and  $K_{IC}$  for the modified resins decreased with increasing functional unit content in the modifiers.

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