

Toughening of Aromatic Diamine-Cured Trifunctional Epoxy Resins by Modification with *N*-Phenylmaleimide–Styrene Copolymers Containing Pendant *p*-Hydroxyphenyl Groups

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SYNOPSIS

N-Phenylmaleimide (PMI)–*N*-(*p*-hydroxy)phenylmaleimide (HPMI)–styrene (St) terpolymers (HPMS), containing pendant *p*-hydroxyphenyl (HP) groups, were prepared and used to improve the toughness of triglycidyl aminocresol epoxy resin cured with *p,p'*-diaminodiphenyl sulfone. HPMS was effective as a modifier for the toughening of the epoxy resin. When using 15 wt % of HPMS (1.0 mol % HP unit, M_w 129,000), the fracture toughness (K_{IC}) for the modified resin increased 190% with a medium loss of flexural strength. The toughening of epoxies could be attained because of the cocontinuous phase structure of the modified resins. The decrease in flexural strength was suppressed to some extent by introducing a functional group into the modifier. The toughening mechanism was discussed in terms of the morphological behavior of the modified epoxy resin system.

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INTRODUCTION

Epoxy resins are one of the most important thermosetting polymers and have wide use as structural adhesives and matrix resin for fiber composites, but their cured resins have one drawback: They are brittle and have poor resistance to crack propagation. The toughness of epoxy resins has been increased by blending with reactive liquid rubbers such as carboxyl-terminated butadiene acrylonitrile rubbers (CTBN).¹ In previous articles, various kinds of epoxide-containing acrylic elastomers have been reported as improving the toughness of *p,p'*-diaminodiphenyl sulfone (DDS)-cured epoxy resins, where vinylbenzyl glycidyl ether and glycidyl (meth)acrylate were used as epoxy-containing monomers.^{2–6}

Engineering thermoplastics are interesting materials as modifiers for epoxy resins from the viewpoint of the maintenance of mechanical and thermal properties for the matrix resins. Modification of

epoxy resins with various types of ductile thermoplastics have been studied as alternatives to reactive rubber for improving the toughness of epoxy resins. At first, commercial poly(ether sulfone)s (PES) such as Victrex were used as modifiers in the modification of polyfunctional epoxies such as tetraglycidyl-4,4'-diaminodiphenyl methane (TGDDM), but less effective owing both to high crosslinking structure and to poor interfacial bonding between two uncompatibilized phases in the cured resin.^{7–9} Terminally functionalized polysulfones are more effective modifiers than are commercial PES.^{10,11} Most recently, polysulfones containing pendant amino groups have been reported as effective modifiers.¹² Other engineering thermoplastics have also been examined as modifiers, where polyetherimides,^{13–16} poly(aryl ether ketone)s,^{17–19} poly(phenylene oxide),^{20,21} and aromatic polyesters^{22,23} have been reported as effective modifiers.

In previous articles, we reported that *N*-phenylmaleimide (PMI)–styrene (St) copolymers (PMS) and PMI–*N*-cyclohexylmaleimide–St terpolymers (PCMS) were effective modifiers for epoxies.^{24–26} It is noteworthy that PMS was effective for toughening of highly crosslinked epoxy matrices such as the

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triglycidyl aminocresol/DDS system.²⁶ PMS and PCMS have no functionalities reacting with epoxide, as reported previously.^{24,25} When using PMS and PCMS as modifiers, fracture toughness (K_{IC}) for the modified resins increased significantly at a medium loss in flexural strength, perhaps because of the physical interfacial adhesion between the epoxy matrix and the modifier. It is well known that the interfacial adhesion is an important factor to obtain effective modifiers for improving the toughness of epoxies.^{1,2} Then, in the previous article, PMI-St-*p*-hydroxystyrene terpolymers (PMSH) were prepared and used as modifiers having reactive groups in the bisphenol A diglycidyl ether (DGEBA)/DDS modification system.²⁷ PMSH had a similar efficiency as a modifier for epoxies to PMS, but was superior to PMS in solvent resistance because of the covalent bond between the epoxy matrix and the modifier-rich phase.

This article reports the modification of DDS-cured triglycidyl aminocresol epoxy resins (TGAC) with highly cross-linked structure by *N*-phenylmaleimide-*N*-(*p*-hydroxy)phenylmaleimide-styrene terpolymers (HPMS) containing functional groups reacting with epoxide. In preliminary experiments, PMSH was degraded based on the basic epoxy groups of TGAC, glycidyl amine types, when dissolved in the epoxy resin at 140°C. Then, HPMS was used as the alternative of PMSH. The effects of the structure and the amount of HPMS added on the toughness of the cured resin were examined.

EXPERIMENTAL

Materials

The epoxy resin was the liquid triglycidyl aminocresol (TGAC) (ELM-100, Sumitomo Chemical Industrial Co., epoxy equivalent weight 113). DDS was used as a curing agent. *N*-phenylmaleimide (PMI) was provided by Nippon Shokubai Corp. and used as received. *N*-(*p*-Hydroxyphenyl) maleimide (HPMI) was supplied by Mitsui Toatsu Fine Corp. and acetylated to obtain *N*-(*p*-acetoxyphenyl)-maleimide (APMI). Styrene was purified in the usual way. Other reagents were used as received.

Measurements

¹H-NMR spectra were recorded on a 90 MHz instrument (JEOL JNM-9MX 90) using DMSO-*d*₆ as the solvent and tetramethylsilane as the internal standard. Molecular weights of the terpolymers were

determined by gel permeation chromatography (Shimadzu LC-5A instrument) using polystyrene standards. Mechanical properties of cured resins were measured with a Shimadzu autograph AGS-500B universal testing machine. Flexural tests were carried out at a crosshead speed of 2 mm/min (JIS K7203). Fracture toughness, K_{IC} , was measured in a three-point bent geometry at a crosshead speed of 1 mm/min (ASTM E-399). Glass transition temperatures (T_g 's) of terpolymers were measured as onset temperatures by differential scanning calorimetry (Shimadzu DSC 41M type) at a heating speed of 10°C/min. The T_g for the TGAC resin was obtained by thermal mechanical analysis (Shimadzu TMA 40M type) 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 -150 and 300°C at a heating speed of 5°C/min at frequency of 1 Hz.

Preparation of *N*-Phenylmaleimide-*N*-(*p*-hydroxyphenyl)maleimide-Styrene Terpolymers

N-Phenylmaleimide-*N*-(*p*-acetoxyphenyl)phenylmaleimide-styrene terpolymers (APMS) were prepared in the 1 : 1 mol ratio of *N*-phenylmaleimides and styrene. The molecular weight of APMS was controlled using dodecanethiol as a chain-transfer agent. A typical procedure of APMS [1 mol % *p*-(acetoxyphenyl) maleimide unit] preparation is as follows:

A flask was charged with PMI (42.5 g, 0.245 mol), APMI (1.16 g, 0.005 mol), St (26.0 g, 0.250 mol), acetone (500 mL), azobisisobutyronitrile (AIBN, 0.82 g, 1 mol %), and dodecanethiol (0.23 g, 0.11 mol %). The flask was purged with N₂ for 0.5 h and a N₂ atmosphere was maintained throughout the polymerization. The polymerization mixture was stirred at 60°C for 5 h. After the polymerization was over, the polymerization mixture was diluted with tetrahydrofuran (THF). Then, the terpolymer was isolated using methanol as the precipitant and purified by reprecipitation with THF/methanol. The white solid polymer was dried *in vacuo* at 60°C and obtained in a quantitative yield.

HPMS was prepared by deacetylation of APMS as follows: A flask was charged with APMS (5 g), dioxane (120 mL), and concentrated HCl (24 mL). The mixtures were stirred at 60°C for 5 h. The polymer mixtures were isolated by using a methanol/hexane (2 : 1 vol ratio) mixture as the precipitant,

washed fully with the precipitant solution, and dried *in vacuo* at 60°C. The crude terpolymer THF solution was purified by pouring into the above precipitant and the isolated polymer was dried *in vacuo* at 60°C.

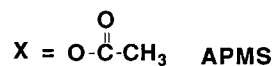
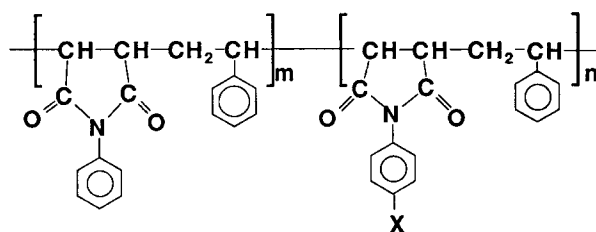
Curing Procedure

The terpolymers were dissolved into the epoxy resin without solvents by heating at 140°C for 4 h. Then, the curing agent, DDS, was added to the mixture, which was kept at 120°C for about 1 h to dissolve DDS. The resulting clean mixture was poured into a silicone rubber mold preheated at 120°C. The curing cycle was 120°C/1 h + 180°C/5 h. DDS was used stoichiometrically to the epoxy resin. The amount (wt %) of the terpolymer used was based on the epoxy resin (TGAC).

RESULTS AND DISCUSSION

Characterization of Terpolymers

APMS was prepared in a quantitative yield (Table I). The molecular weights of APMS were controlled by using dodecanethiol as a transfer agent. The terpolymer compositions were equal to the feed compositions by ¹H-NMR spectroscopy. It is well known that the radical copolymerization of PMI and St gives alternating copolymers.²⁸ The terpolymerization of PMI, APMI, and St must also afford alternating copolymers composed of both PMI–St and APMI–St units. HPMS was prepared by deacetylation of APMS (Scheme 1). The weight-average molecular weight (M_w) was used as a measure of



Scheme 1

the molecular weight (M_w) of HPMS and the M_w dependence of physical properties for the modified resins could be discussed by using M_w , independent of the molecular weight distribution as reported previously.^{24–26} Table II reports some characteristic properties of HPMS. In spite of the carbon–carbon single-bond repeating units, HPMS has a high T_g of over 215°C as well as does PMS and PCMS, 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 and HPMS as reported previously.²⁹

Mechanical and Thermal Properties of Modified Epoxy Resins

It is well known that phenolic groups react with epoxide in the presence of tertiary amines to form the

Table I Preparation and Characterization of APMS^a

Entry No.	Feed Composition ^b			$\text{C}_{12}\text{H}_{25}\text{SH}^c$ (Mol %)	Yield (%)	M_w^d (10 ⁴)	M_n^d (10 ⁴)	M_w/M_n	T_g^e (°C)
	PMI	APMI	St						
APMS4	49	1	50	0.40	95	8.0	2.9	2.74	216
5	49	1	50	0.23	96	12.1	4.2	2.87	—
1	49	1	50	0.08	95	19.9	6.2	3.23	221
3	49	1	50	0.025	95	29.6	9.1	3.25	222
6	48	2	50	0.23	97	10.9	3.5	3.10	—
2	48	2	50	0.07	96	21.2	6.7	3.17	—
7	47	3	50	0.20	95	12.1	4.9	3.75	—

^a Polymerization conditions; 60°C, 5 h in acetone.

^b Mol %.

^c Chain-transfer agent.

^d By GPC.

^e By DSC.

Table II Characterization of HPMS^a

Entry No.	Modifier Composition ^b				M_w^d (10 ⁴)	M_n^d (10 ⁴)	M_w/M_n	T_g^e (°C)
	No. ^c	PMI	HPMI	St				
HPMS4	APMS4	49	1	50	7.9	2.9	2.71	216
5	5	49	1	50	12.9	5.1	2.52	219
1	1	49	1	50	20.1	6.3	3.21	221
3	3	49	1	50	29.2	8.1	3.61	220
6	6	48	2	50	11.1	4.0	2.79	221
2	2	48	2	50	22.0	6.8	3.22	222
7	7	47	3	50	11.9	4.1	2.98	224

^a Reaction conditions; at 60°C for 5 h in dioxane.

^b Mol %.

^c Entry number in Table I.

^d By GPC.

^e By DSC.

adducts.³⁰ In this study, the curing was carried out without catalysts, as the TGAC epoxy resin used has tertiary amino units. The cured parent epoxy resin was transparent. The modified resins became translucent during curing.

Figures 1 and 2 show the mechanical and thermal properties of the modified resins as a function of concentration of the modifiers. HPMS having a M_w of ca. 200,000 was used based on the previous results in the modification of the TGAC/DDS system with PMS²⁶; the optimum composition for modification

was an inclusion of 15 wt % of PMS with M_w 214,000, where K_{IC} for the modified resin increased 100%. The K_{IC} values for the HPMS (1.0 mol % *N*-(*p*-hydroxy)phenylmaleimide (HP) unit, M_w 201,000)-modified resins increased discontinuously

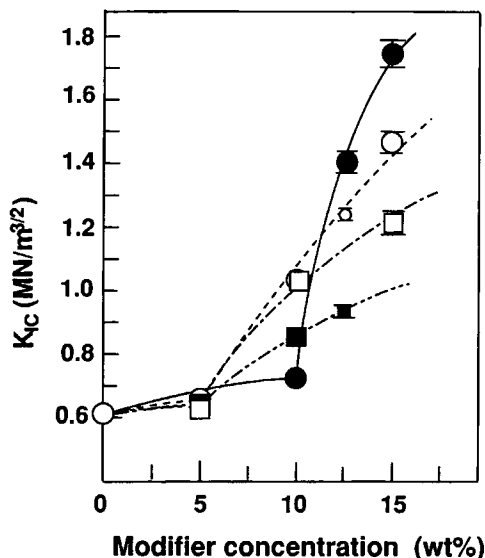


Figure 1 Fracture toughness for the modified resins as function of HPMS concentration: (●) control; (○) HPMS (1 mol % HP unit, M_w 201,000); (■) HPMS (2 mol % HP unit, M_w 220,000); (●) HPMS (1 mol % HP unit, M_w 129,000); (□) PMS (M_w 214,000).

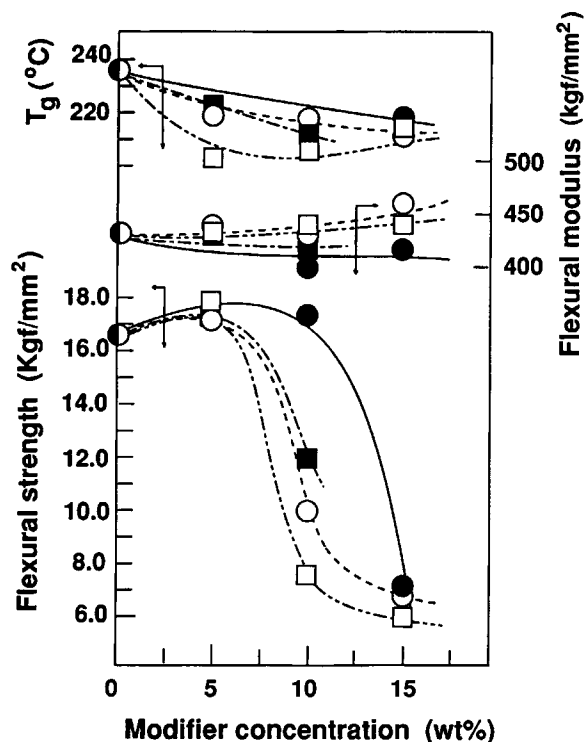


Figure 2 Physical properties for the modified resins as function of HPMS concentration: (●) control; (○) HPMS (1 mol % HP unit, M_w 201,000); (■) HPMS (2 mol % HP unit, M_w 220,000); (●) HPMS (1 mol % HP unit, M_w 129,000); (□) PMS (M_w 214,000).

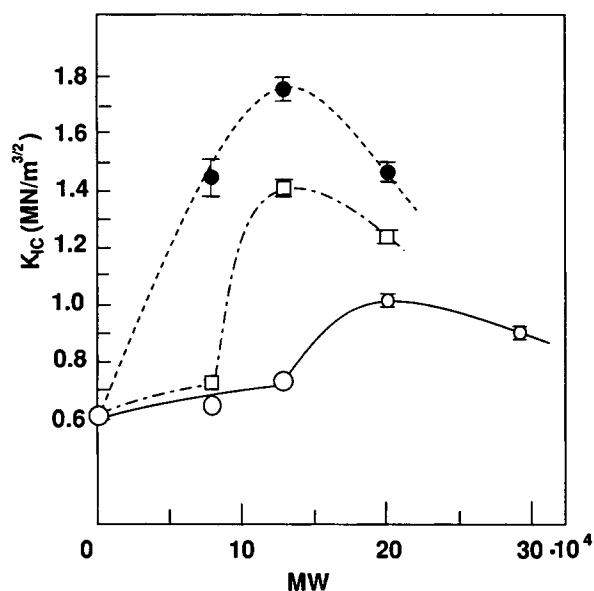


Figure 3 Dependence of fracture toughness for the modified resins on HPMS (1 mol % HP unit) molecular weight: (●) control; (○) 10 wt % addition; (□) 13 wt % addition; (●) 15 wt % addition.

with increasing HPMS concentration (Fig. 1). When using 15 wt % of HPMS (1.0 mol % HP unit, M_w 201,000), K_{IC} for the modified resin increased 140%, compared to that for the unmodified resin, which indicates that HPMS (1.0 mol % HP unit) was more effective than was PMS. HPMS (M_w 220,000) having a 2.0 mol % HP unit was less effective than either PMS (M_w 214,000) and HPMS (M_w 201,000) with a 1.0 mol % HP unit.

The decrease in the flexural strength for the modified resins was inversely proportional to the increase in K_{IC} (Fig. 2). The flexural moduli for thmodified resins were comparable or larger compared to that for the unmodified resin except for the HPMS (1.0 mol % HP unit, M_w 129,000), where the flexural moduli were slightly lower. T_g 's for the modified resins were lower than that for the unmodified resin. The fracture results in the modification with low M_w HPMS (1.0 mol % HP unit, M_w 129,000) was unexpected and interesting; on 10 wt % addition, the increase in K_{IC} was small, but for more than 13 wt % addition, K_{IC} for the modified resin increased abruptly. Lower M_w HPMS (1.0 mol % HP unit, M_w 129,000) was more effective than were the others and its use led to a 190% increase in K_{IC} on 15 wt % addition. The toughening of epoxies could be attained because of a cocontinuous phase structure as shown in the morphological results (Fig. 6).

Then, the HPMS M_w dependence of K_{IC} for the modified resins was investigated in detail on incorporation of HPMS having 1.0 mol % HP unit (Fig. 3). On addition of 10 wt % of HPMS, K_{IC} for the modified resin increased discontinuously with an increase in HPMS M_w . This fracture behavior was similar to that in the modification of the TGAC/DDS system with PMS.²⁶ Lower M_w HPMS (1.0 mol % HP unit, M_w 129,000) became the most effective modifier on addition of more than 13 wt % and K_{IC} for the modified resin increased 190% on 15 wt % addition. The flexural strength for the modified resins decreased with increasing K_{IC} . The flexural moduli for the modified resins were comparable or larger, compared to that for the parent epoxy resin. T_g 's for the modified resins were slightly low, compared to that for the parent resin (Fig. 4).

Figure 5 shows the terpolymer structure dependence of the mechanical and thermal properties for the modified resins on 15 wt % addition; HPMS having lower M_w (M_w ca. 120,000) was used on the basis of the above results on the HPMS M_w dependence of K_{IC} (Fig. 3). K_{IC} for the modified resins showed the maximum value with increasing HP units in the terpolymers and HPMS (M_w 129,000) with the 1.0 mol % HP unit was more effective. The

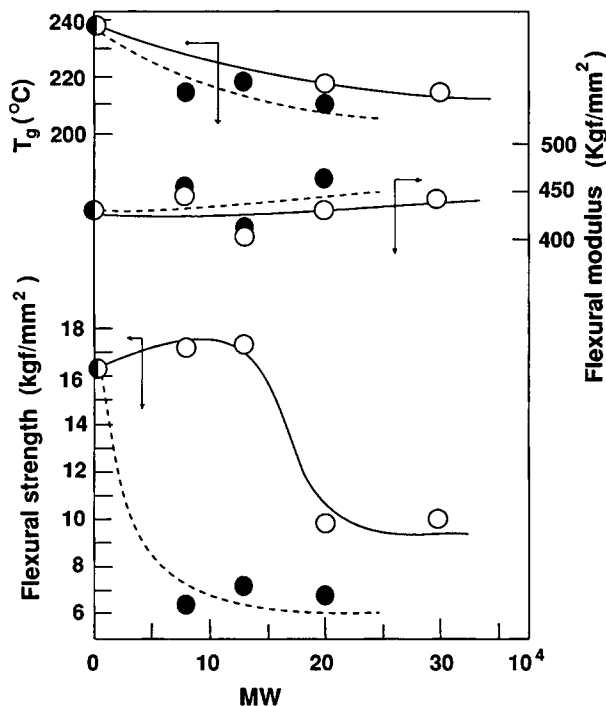


Figure 4 Dependence of physical properties for the modified resins on HPMS (1 mol % HP unit) molecular weight: (●) control; (○) 10 wt % addition; (●) 15 wt % addition.

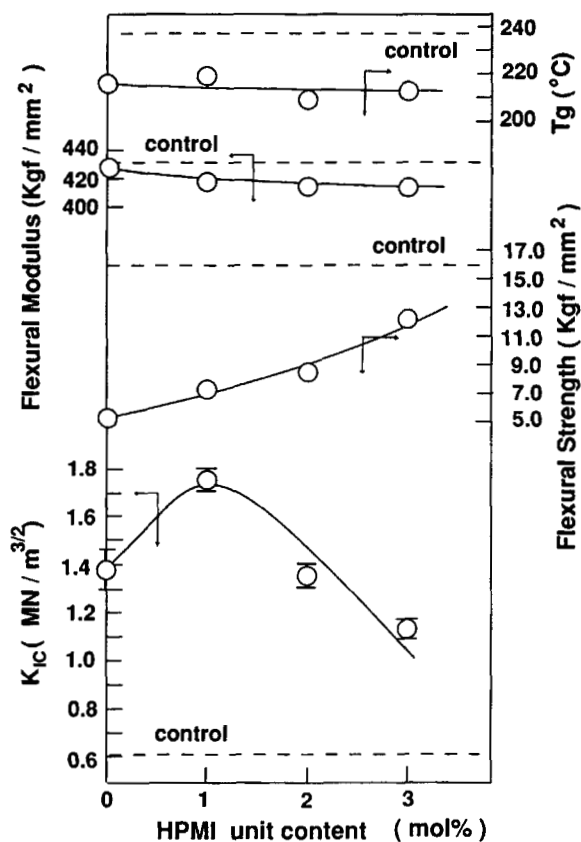


Figure 5 Dependence of physical properties for the modified resins on the modifier structure in the modification with 15 wt % of the modifier.

flexural strength for the modified resins increased with increasing HP units in the terpolymers and flexural moduli decreased slightly. K_{1c} for the HPMS (2 mol % HP unit)-modified resin was similar to that for the PMS-modified material, but the flexural strength for the former resin was larger than that for the latter one. These results show that HPMS having the 1 mol % HP unit was more effective than was PMS and that the decrease in flexural strength was suppressed to some extent by introducing functional groups in the modifier. T_g 's for the modified resins were almost equal to that for the PMS-modified resin, but lower than that for the unmodified resin.

Morphologies of the Modified Epoxy Resins

The morphologies of the cured resins were investigated by the scanning electron micrographs (SEMs). Figures 6–9 show SEMs of fracture surfaces for the modified resins that failed in the unstable crack propagation stages. The parent epoxy resins had only one phase, as reported previously.²

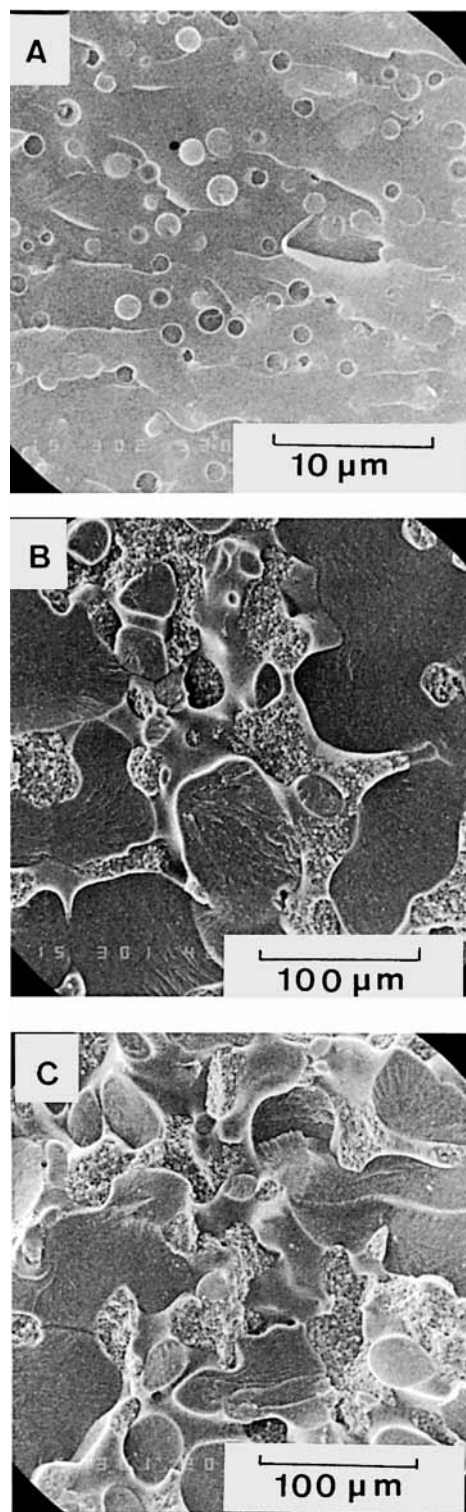


Figure 6 SEMs of fracture surfaces for the HPMS-modified resins. Amount of HPMS (1 mol % HP unit, M_w 129,000): (A) 10 wt % addition; (B) 13 wt % addition; (C) 15 wt % addition.

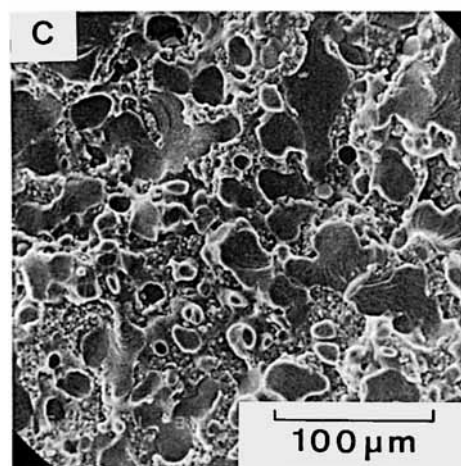
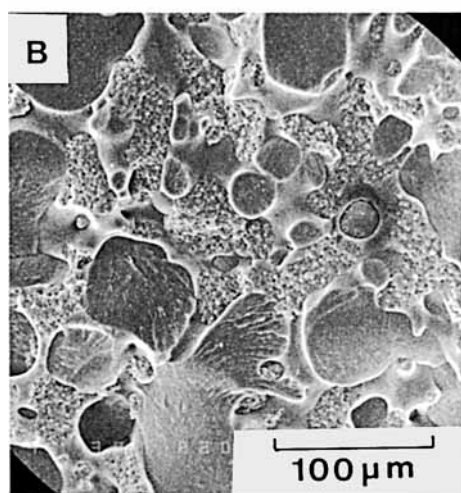
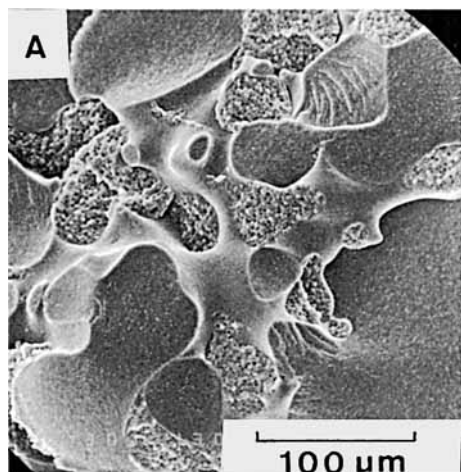


Figure 7 SEMs of fracture surfaces for the cured resins modified with 15 wt % of HPMS (1 mol % HP unit): (A) M_w 79,200; (B) M_w 129,000; (C) M_w 201,000.

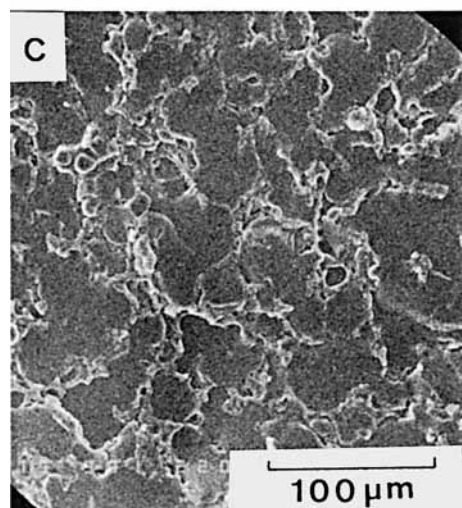
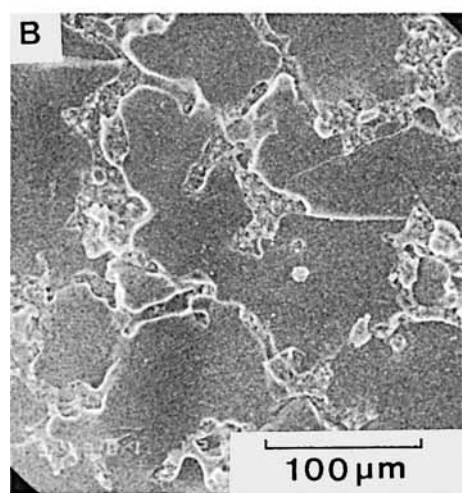
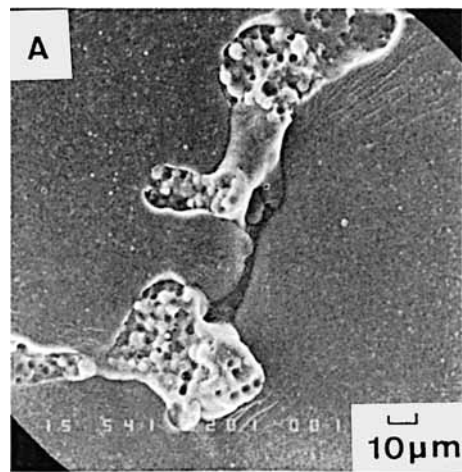


Figure 8 SEMs of fracture surfaces for the cured resins modified with 10 wt % of the modifiers: (A) PMS (M_w 214,000); (B) HPMS (1 mol % HP unit, M_w 201,000); (C) HPMS (2 mol % HP unit, M_w 220,000).

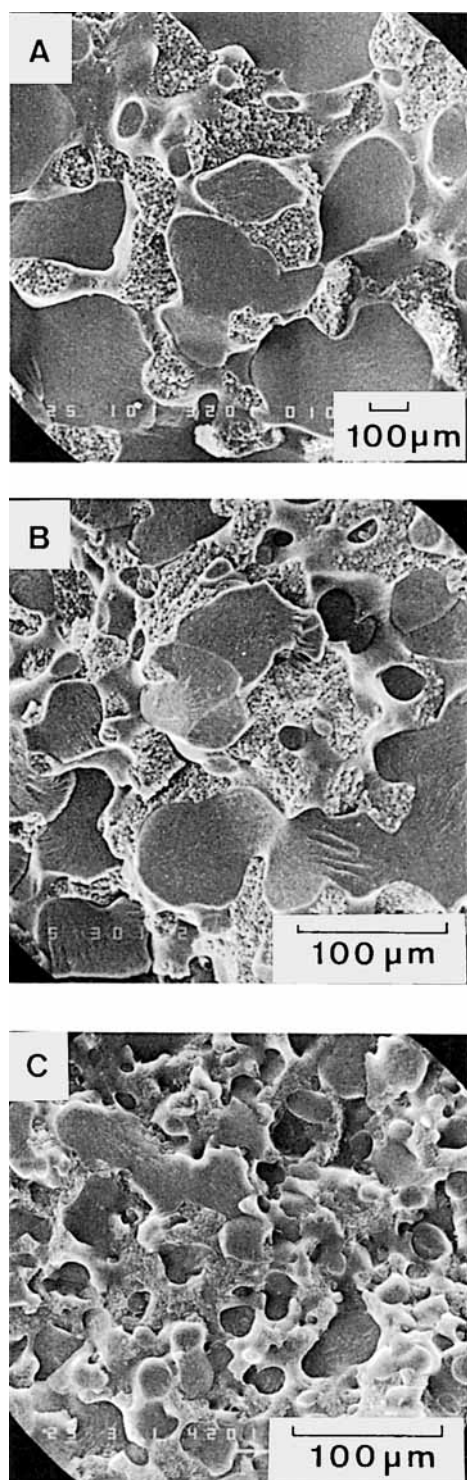


Figure 9 SEMs of fracture surfaces for the cured resins modified with 15 wt % of the modifiers: (A) PMS (M_w 109,000); (B) HPMS (1 mol % HP unit, M_w 129,000); (C) HPMS (2 mol % HP unit, M_w 111,000).

Inclusion of HPMS led to two-phase morphology. The morphologies of the cured resins changed drastically, dependent on the concentration of HPMS. In the modification with 10 wt % of HPMS (1 mol % HP unit, M_w 129,000), the modified resin had a two-phase morphology with HPMS-rich spherical particles dispersed in the epoxy-rich matrix [Fig. 6(A)]; the volume fraction and the average diameter of the particle were 0.151 and 0.90 μm , respectively. On addition of more than 13 wt % of the same modifier, the modified resins had cocontinuous phase morphologies [Fig. 6(B) and (C)], where the toughness of epoxies could be improved significantly (Fig. 1).

On 15 wt % addition of HPMS (1.0 mol % HP unit), morphologies of the cured resins showed cocontinuous phase structures (Fig. 7). The dark and smooth epoxy-rich matrix tended to become small with an increase in HPMS M_w . These morphologies indicate that the larger the HPMS M_w the more the epoxy matrix was incorporated into the HPMS-rich phase by chemical blending. When using higher M_w HPMS (1.0 mol % HP unit, M_w 201,000), the morphology of the modified resin was different from those of the lower M_w HPMS-modified resins and the epoxy-rich phase tended to form somewhat irregular particles. This morphology might be an intermediate structure from a cocontinuous phase to a phase-inverted structure. The K_{IC} value for the high M_w HPMS (M_w 201,000)-modified resin is lower than that for the lower M_w HPMS (M_w 129,000)-modified material.

Figure 8 shows the dependence of morphology for the modified resin on the modifier structure in the use of 10 wt % of higher M_w modifier; the morphology of the PMS-modified resin was reported in a previous article.²⁶ The modified resins had cocontinuous phase morphologies. The extent of dispersion of the modifier-rich phase became higher with increasing functional groups in the modifier. These results indicate that the compatibility of HPMS with the epoxy matrix increased with increasing HPMI units in the modifier.

In the modification systems with 15 wt % of lower M_w modifiers, morphologies for the cured resins also depended on the modifier structure. In the modification with PMS or HPMS (1.0 mol % HP unit), morphologies of the cured resins showed cocontinuous phase structures and the extent of dispersion of the cocontinuous phase for the HPMS-modified resin was higher than that for the PMS-modified material [Fig. 9(A) and (B)]. On 15 wt % addition of HPMS (2.0 mol % HP unit), the epoxy-rich phase tended to coagulate and form a phase-inversion

structure [Fig. 9(C)], where small coagulated epoxy-rich domains in the HPMS-rich phase became somewhat undefined, perhaps because of chemical reaction of HPMS and epoxies.

To examine the interfacial adhesion between the HPMS-rich phase and the TGAC epoxy matrix, THF-etching of fracture surface was carried out at room temperature for 72 h. The HPMS-rich phase could not be removed by THF because of the chemical reaction of HPMS and the epoxy groups. In the modification with PMS having no functionalities, the PMS-rich phase could be clearly removed, as reported previously.²⁴

Dynamic Viscoelastic Analysis of Modified Epoxy Resins

Dynamic viscoelastic analysis can give information on the microstructure of cured resins. Figures 10–12 show the storage moduli, G' , and $\tan \delta$ curves for the unmodified and modified resins. On 10 wt % addition of HPMS (1.0 mol % HP unit, M_w 129,000), the peak position of the α -relaxation in the $\tan \delta$ curve shifted slightly toward lower temperature and their magnitude became larger, compared to dynamic viscoelastic behavior for the parent epoxy resin and a shoulder peak appeared at ca. 210°C (Fig. 10). On 15 wt % addition, the α -relaxation peak position shifted toward that for the unmodified resin

and a well-defined α' -relaxation peak was observed at 225°C. The appearance of the new α' -relaxation peak in the $\tan \delta$ curve indicates the presence of the phase-separated structure for the modified resin in the present modification system. These results corresponds to the morphological results (Fig. 6).

In the modification with 10 wt % of the modifiers having similar M_w (ca. 200,000), the peak positions of the α -relaxation in the $\tan \delta$ curve for the HPMS (1 mol % HP unit)-modified resin shifted toward lower temperature and the α -relaxation peaks became shoulder, compared to the dynamic viscoelastic behavior for the PMS-modified resin (Fig. 11). This behavior indicates that some of HPMS were incorporated into the epoxy matrix and that the HPMS-rich phase contained the epoxy matrix by chemical blending. Higher M_w HPMS with the 2 mol % HP unit had higher compatibility with the epoxy matrix and the α -relaxation peak became smaller than with the others. The change in compatibility corresponds to the morphological behavior of the modified resin; the extent of dispersion of the cocontinuous phase became higher with increasing the functional group content in the modifiers (Fig. 8).

On 15 wt % addition of low M_w HPMS (1.0 mol % HP unit, M_w 129,000), the peak position of the α -relaxation in the $\tan \delta$ curve hardly changed and their magnitudes became larger, compared with dynamic viscoelastic behavior for the parent epoxy

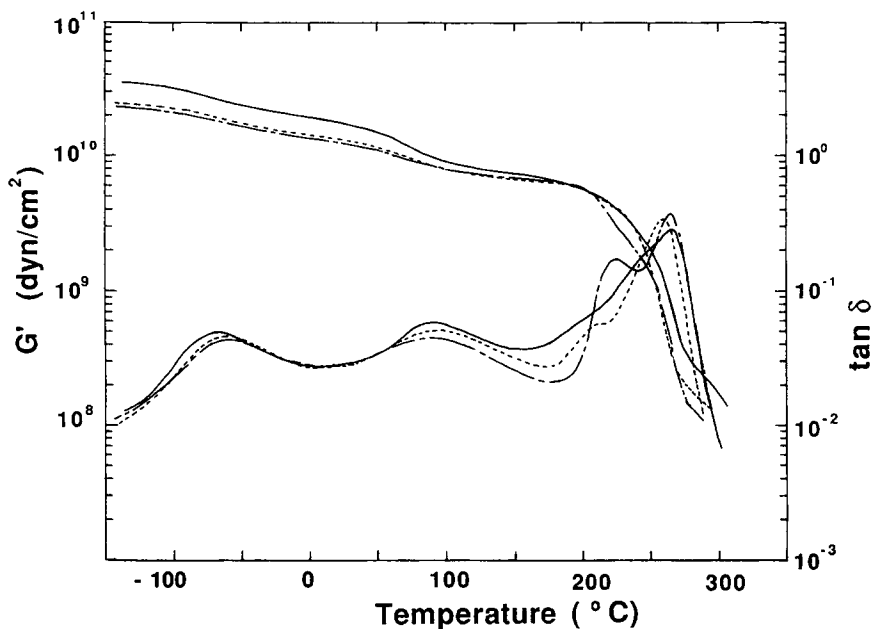


Figure 10 Dynamic viscoelastic analysis for unmodified and HPMS-modified resins: HPMS (1 mol % HP unit, M_w 129,000): (—) 0 wt % (control); (-----) 10 wt %; (- - -) 15 wt %.

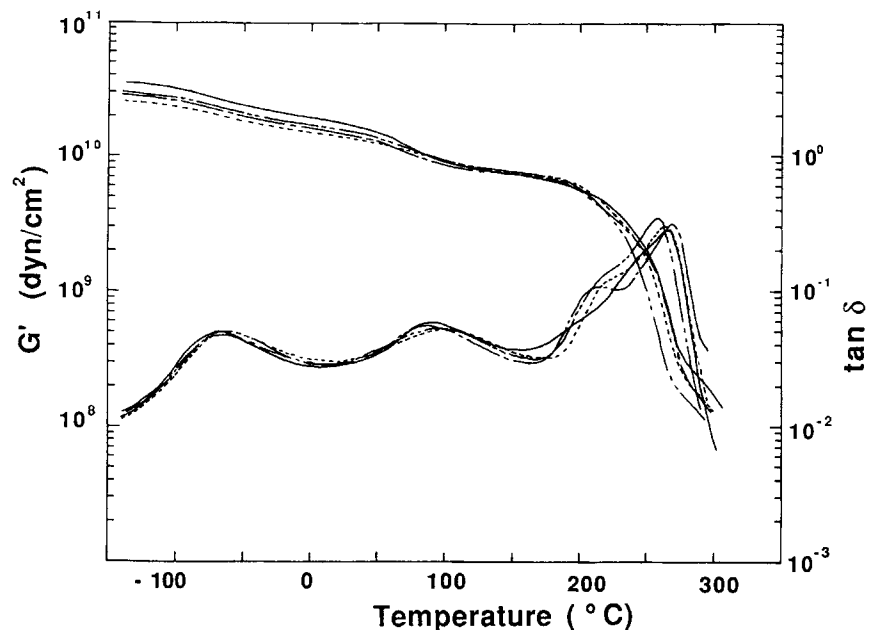


Figure 11 Dynamic viscoelastic analysis for unmodified and modified resins. The modifier 10 wt % addition: (—) control; (---) PMS (M_w 214,000); (- · - ·) HPMS (1 mol % HP unit, M_w 201,000); (·····) HPMS (2 mol % HP unit, M_w 220,000).

resin (Fig. 12). When using 15 wt % of HPMS (2.0 mol % HP unit, M_w 111,000) the α -relaxation peak position shifted slightly toward lower temperature. The α' -relaxation peak was observed at 225°C in the modification with HPMS having the 1.0 mol % HP

unit as well as in the PMS (M_w 109,000) modification, but a α' -relaxation peak became the shoulder in the use of HPMS with higher OH content (HP 2.0 mol %). These results show that compatibility of HPMS and the epoxy matrix increases with in-

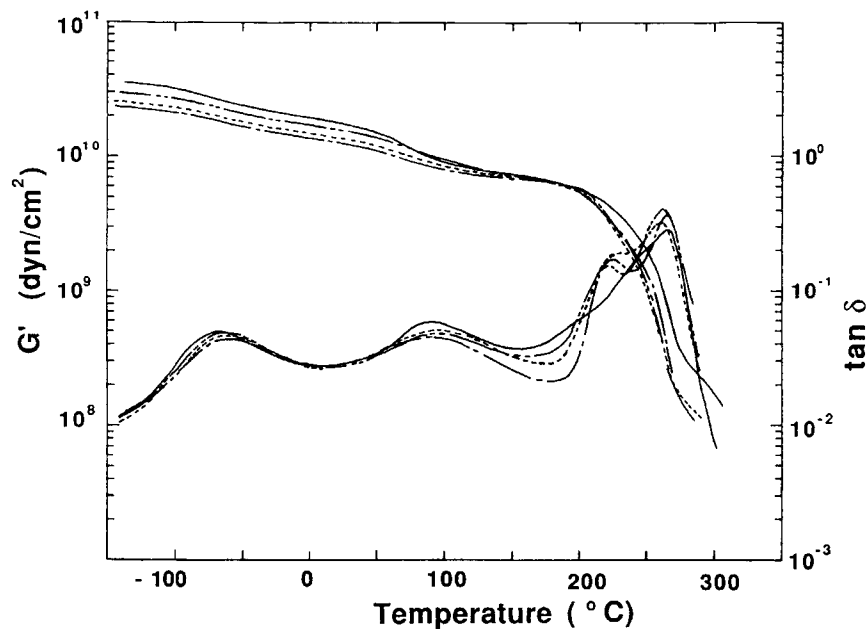


Figure 12 Dynamic viscoelastic analysis for unmodified and modified resins. The modifier 15 wt % addition: (—) control; (---) PMS (M_w 109,000); (- · - ·) HPMS (1 mol % HP unit, M_w 129,000); (·····) HPMS (2 mol % HP unit, M_w 111,000).

creasing the functional group in HPMS. These dynamic viscoelastic behaviors correspond to the morphologies of the modified resins; the morphology of the HPMS (2 mol % HP unit)-modified resin was different from the others (Fig. 9).

The storage moduli for the modified resins at room temperature decreased in every case, compared to that for the unmodified resin.

Discussion on the Toughening Mechanism

HPMS was an effective modifier for improvement in the toughness of the highly crosslinked epoxy resins and its efficiency was higher than that of PMS.²⁶ The toughening mechanism could be discussed in terms of the morphological behavior for the modified resins. The interesting and characteristic results in the relationship between the toughness and the morphology of the modified epoxy resins were as follows:

In the present modification system, the toughness of epoxies could be achieved based on the cocontinuous phase structure, where fracture energy could be dissipated due to ductile drawing and tearing of the HPMS-rich phases. For example, when using 10 wt % of lower M_w HPMS (1 mol % HP unit), the modified resin had the particulate morphology and the increase in K_{IC} was rather lower, but inclusion of more than 13 wt % of HPMS led to the cocontinuous phase morphologies of the modified resins with the significant increase in K_{IC} (Figs. 1 and 6).

In the modification with 15 wt % of HPMS having the 1 mol % HP unit, the extent of dispersion of the cocontinuous phase became higher with increasing M_w of the terpolymers, but the increase in K_{IC} was not proportional to the increase in dispersibility (Figs. 3 and 7). Such morphological behaviors were also observed on both 10 wt % addition of high M_w terpolymers and 15 wt % addition of low M_w terpolymers (Figs. 8 and 9), where the extent of dispersion of the cocontinuous phase became higher with increasing the functional unit in the modifier, but the increase in dispersibility did not correspond to the improvement in toughness (Figs. 1 and 5).

These results indicate that there is the optimum extent of dispersion of the cocontinuous phase to improve the brittleness of epoxies in the present modification. It is thought that the increase in the interfacial adhesion based on the introduction of the functionality may be favorable to obtain an effective modifier, but the higher extent of dispersion of the cocontinuous phase based on the increase in compatibility by chemical blending may be unfavorable

in the present modification and that the efficiency of HPMS as the modifier may be compensated by these adverse effects. These results were unexpected because it was thought that the cocontinuous phase structure with a shorter periodic distance (high dispersibility of the continuous phase) would be the desired one to obtain high effective modifiers: a great increase in K_{IC} with retaining the physical properties for the modified resin, as shown below. But it is noteworthy that HPMS having the 1 mol % HP unit is more effective as the modifier than is PMS because of chemical blending.

The reaction-induced phase separation by the spinodal decomposition was investigated in the DGEBA/*p,p'*-diaminodiphenyl methane/PES modification.³¹ During curing, the increase in M_w of epoxy oligomers initiates phase separation. Morphology depends on the curing conditions as phase separation competes with gelation or vitrification. The PES-modified resins had particulate, cocontinuous, or phase-inverted morphologies, depending on both the resin compositions and the curing conditions. After curing under the mild reaction conditions, the modified resin had a cocontinuous structure with a short periodic distance (the higher extent of dispersion of the PES-rich phase) and the excellent adhesion properties could be attained by the phase-inversion structure (the connected global structure). Most recently, the effect of the morphology on the fracture toughness of the modified resins was investigated in the TGDDM/DDS/phenolic hydroxyl-terminated polysulfone modification.³² Morphology was controlled by changing the curing conditions and the phase-inverted structure was a optimum structure for toughening.

CONCLUSION

HPMS having phenolic hydroxyl groups was an effective modifier for improving the toughness of highly crosslinked epoxy matrix and its efficiency was higher than that of PMS. The most effective modification could be attained based on the cocontinuous structure of the modified resin. When using 15 wt % of HPMS (1.0 mol % HP unit, M_w 129,000), the K_{IC} for the modified resin increased 190% with retention in flexural modulus and T_g . The decrease in flexural strength was suppressed to some extent by introducing the functional group in the modifier. In the modification with HPMS (2.0 mol % HP unit, M_w 111,000), the K_{IC} for the modified resin was similar to that for the PMS-modified resin and flexural strength was restored to some extent. The use

of HPMS as the modifier led to the modified resin with balanced physical properties. The solvent resistance of the modified epoxy resins could also be improved by introducing the functional group into the modifiers.

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