Effect of Matrix Compositions on Modification of Bismaleimide Resin by N-Phenylmaleimide–Styrene Copolymers

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SYNOPSIS

The effect of matrix compositions on the toughening of bismaleimide resin by modification with N-phenylmaleimide–styrene copolymers (PMS) were examined. The bismaleimide resin was composed of 4,4'-bismaleimidediphenyl methane (BMI), o,o'-diallyl bisphenol A (DBA), and triallyl isocyanurate (TAIC). The matrix structure was controlled by changing the equivalent ratio of the two allyl components (DBA and TAIC). Morphologies of the modified resins changed from particulate to cocontinuous and to inverted phase structures, depending on the modifier content. The most effective modification for the cured resins could be attained because of the cocontinuous structure of the modified resins. Inclusion of TAIC led to a decrease in the extent of dispersion of the cocontinuous phase, and the optimum matrix structure to improve the toughness was obtained on 20 eq % addition of TAIC. For example, when using 20 eq % of TAIC and 5 wt % of PMS (M_w 303,000), the fracture toughness (K_{IC}) for the modified resins increased 100% at a moderate loss of flexural strength and with retention in flexural modulus and the glass transition temperature, compared to those of the unmodified cured Matrimid resin. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Addition polyimide resins are one of the most important thermosetting polymers and have received attention because of their high thermal stability and mechanical properties. The drawback of the polyimide resins is that they are brittle and difficult to process. Bismaleimide resins were also investigated because of their good processability and nonvolatility. Recently a two-component bismaleimide system (Matrimid 5292 A and B), composed of 4,4'-bismaleimidediphenyl methane (BMI) and o,o'-diallyl bisphenol A (DBA), was developed by Ciba Geigy Corp. to improve mechanical properties and processability.[1] DBA copolymerizes with BMI via an ene reaction during curing. The brittleness of the cured resin was improved compared

to the conventional bismaleimide resins, but its fracture toughness is not yet sufficient for use as the composite matrix.

The toughness of epoxy resins was increased by blending with reactive liquid rubbers such as carboxyl-terminated butadiene acrylonitrile rubbers (CTBN)[2] or engineering thermoplastics, for example, polysulfones[3-5] or poly(ether imide),[6-8] etc. Engineering thermoplastics are interesting materials as modifiers for bismaleimide resins from the viewpoint of the maintenance of mechanical and thermal properties for the matrix resins. Modification of the bismaleimide resin (the Matrimid 5292 system) was carried out based on information on the toughening of epoxies by thermoplastics in our laboratory.[9-12] In previous articles we reported that N-phenylmaleimide–styrene copolymer (PMS) was an effective modifier for both the epoxy[13,14] and the bismaleimide resins.[15] N-phenylmaleimide-N-cyclohexylmaleimide–styrene terpolymer was also effective as a modifier for the epoxy.[16] Recently N-phenylmaleimide–

styrene-_p_-hydroxystyrene terpolymers (PMSH) having functionalities was also an effective modifier for epoxies.[17]

This article reports the effect of matrix compositions on the modification of the bismaleimide resin (the Matrimid 5292 A/B system) by PMS. The matrix structure was controlled by using triallyl isocyanurate (TAIC) as a component of the allyl compounds. TAIC was incorporated into the bismaleimide matrix via the ene reaction. The structures of BMI (Matrimid 5292A), DBA (Matrimid 5292B), and TAIC are shown in Scheme 1.

EXPERIMENTAL

Materials

The bismaleimide resin was a commercial product composed of BMI and DBA (Matrimid 5292 A/B). The low viscous liquid TAIC was supplied by Nippon
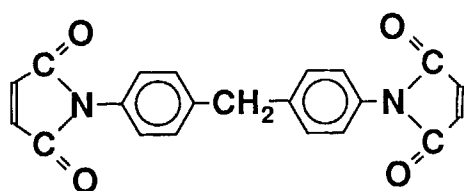

Matrimid 5292A

Matrimid 5292B

Triallyl isocyanurate

Scheme 1

Kasei Chem. Ind. Corporation. _N_-phenylmaleimide was provided by Nippon Shokubai Corp. and used as received. Styrene was purified in the usual way. PMS was prepared as reported previously.[13] Other reagents were used as received.

Measurements

^{1}H-NMR spectra were recorded on a 90-MHz instrument (JEOL JNM-9MX 90) at 60°C using CDCl$_3$ as solvent and tetramethylsilane as internal standard. The molecular weight of PMS was measured by gel permeation chromatography (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 bend geometry at a crosshead speed of 1 mm/min (ASTM E-399). The glass transition temperatures (T_gs) of PMS and cured resins were measured as the onset temperatures by differential scanning calorimetry (DSC, Shimadzu DSC 41M type) at a heating speed of 10°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 (Rheometrics Co.) between −50 and 400°C at a heating speed of 5°C/min at frequency of 1 Hz.

Curing Procedure

PMS were dissolved into DBA at 160°C without solvents. Then BMI was added to the mixture, which was kept at 130°C to dissolve BMI. The resulting clean mixture was degassed _in vacuo_ at 130°C and then low viscous TAIC was added at 130°C. BMI and two allyl components (DBA and TAIC) were used in an equivalent ratio of 1 : 1. The mixture was poured into molds and preheated at 130°C to obtain 4 or 7 mm thick plaques. The mold consisted of one pair of upright and metal crip-held glass 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 160°C/5 h + 180°C/5 h + 200°C/2 h + 250°C/6 h. After curing the oven temperature was decreased gradually from 250°C to room temperature, and the time taken to reach 50°C was about 5 h.
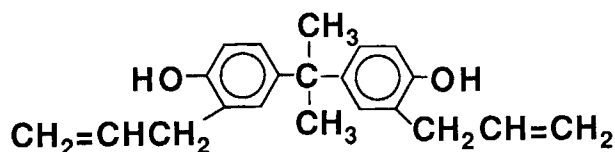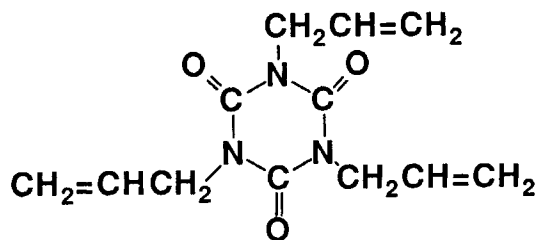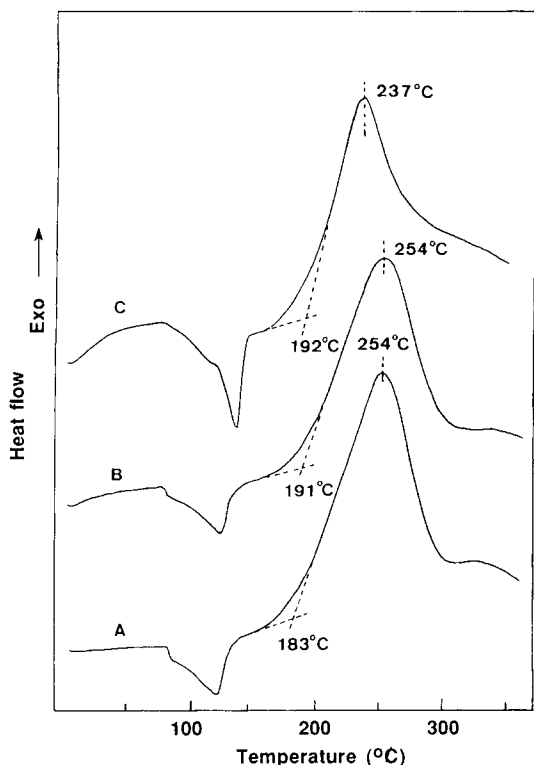
Figure 1   DSC traces of bismaleimide resins: (A) BMI + DBA (1 : 1 eq. ratio); (B) BMI + DBA + TAIC (1 : 0.8 : 0.2 eq. ratio); (C) BMI + TAIC (1 : 1 eq. ratio).

RESULTS AND DISCUSSION

Mechanical and Thermal Properties of Modified Bismaleimide Resins

The cure reactions of the bismaleimide resins were examined by DSC as a function of matrix compo-

sitions. Samples for DSC measurements were prepared by mixing BMI and allyl components at 80°C. Figure 1 shows DSC traces of the bismaleimide resins. The curing behaviors below 145°C were obscure because of overlapping with the endothermic peak based on melting of some dispersed BMI. But the exothermic behaviors between 150 and 300°C were rather similar to each other, independent of the matrix compositions. In the temperature region the ene reaction of maleimide and allyl units is reported to be significant.[1,18] Then it is thought that the ene reactivities of allyl units in TAIC is similar to those in DBA.

PMS, the modifier, was prepared in a quantitative yield. The molecular weight of PMS could be controlled by using dodecanethiol as a chain transfer agent. The copolymer composition was equal to the feed composition by ^{1}H-NMR spectroscopy. It is well known that the radical copolymerization of PMI and styrene gives alternating copolymers.[19] In spite of the carbon–carbon single bond repeating units, PMS has high T_g of ca. 220°C, because the bulkiness of two side groups prevents the molecular motion of the main chain. In this study PMS having M_w ca. 300,000 was used based on the previous results in the modification of the bismaleimide resin with PMS.[15] The characterization of PMS is shown in Table I.

Table I shows the representative results for the modification of the bismaleimide resin with PMS. The unmodified bismaleimide resin was transparent. The modified resins became translucent during curing. The curing conditions (160°C/5 h + 180°C/5 h + 200°C/2 h + 250°C/6 h) in this study were slightly

Table I   Physical Properties of Modified Bismaleimide Resins

Entry No.	Matrix Composition BMI : DBA : TAIC (mol % ratio)	TAIC Content (eq %)	PMS[a] Content (wt %)	K_{IC} (MPa m$^{1/2}$)	n[b]	Flexural Properties Strength (MPa)	Modulus (GPa)	n[b]	T_g[c] (°C)
Control A	1.00 : 1.00 : 0	0	0	0.67 ± 0.01	9	182 ± 8	3.94 ± 0.03	9	285
Control B	1.00 : 0.80 : 0.13	20	0	0.70 ± 0.02	13	181 ± 10	4.06 ± 0.05	13	286
12	1.00 : 1.00 : 0	0	5.0	1.17 ± 0.02	7	126 ± 8	3.92 ± 0.03	6	283
13	1.00 : 0.90 : 0.07	10	5.0	1.25 ± 0.03	6	108 ± 2	3.84 ± 0.06	7	287
07	1.00 : 0.80 : 0.13	20	2.5	0.89 ± 0.04	7	180 ± 7	3.91 ± 0.03	6	286
10	1.00 : 0.80 : 0.13	20	4.5	1.29 ± 0.02	5	124 ± 7	3.89 ± 0.05	7	283
08	1.00 : 0.80 : 0.13	20	5.0	1.33 ± 0.02	6	110 ± 5	3.88 ± 0.08	9	281
14	1.00 : 0.70 : 0.20	30	5.0	1.14 ± 0.02	6	91 ± 2	3.90 ± 0.06	7	289

Values are mean ± SD.
[a] PMS, M_w 303,000, M_n 117,000, T_g 221°C.
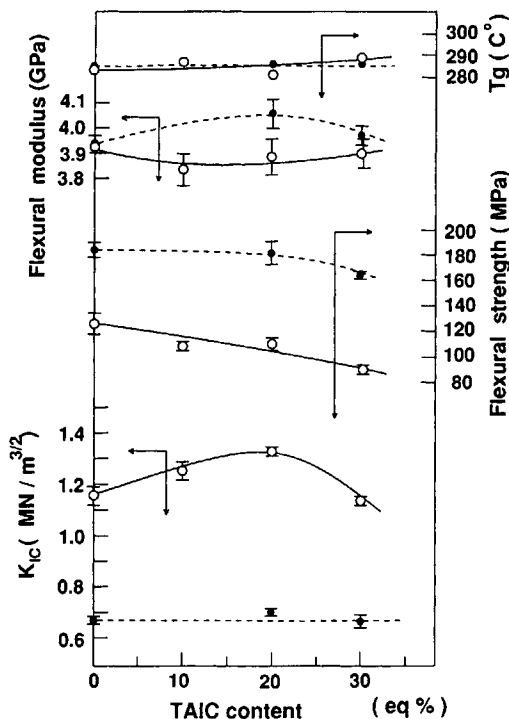[b] Specimen number.
[c] By DSC.

Figure 2 Dependence of physical properties for the modified resins on the matrix compositions in the modification with 5 wt % of the modifier: (●) the unmodified resins and (○) the modified resins.

different from those (160°C/3 h + 180°C/1 h + 200°C/2 h + 250°C/6 h) in the modification of the Matrimid 5292 system with PMS in the previous article,[15] because the modifier, PMS, phase separated macroscopically in the present modification containing TAIC, when cured under the latter conditions. This indicates low compatibility of PMS with the bismaleimide matrix containing TAIC.

Figure 2 shows the effect of the matrix compositions on the mechanical and thermal properties of the cured resins. The K_{IC} for the unmodified resins was hardly independent of the matrix compositions. Flexural strength for the unmodified resin decreases slightly on 30 eq % addition of TAIC, and flexural moduli were comparable or larger than that for the cured Matrimid resin. T_gs for the unmodified resin did not decrease by using TAIC. When using 5 wt % of PMS (M_w 303,000), the K_{IC} values for the modified resins increased gradually up to 20 eq % addition of TAIC and then decreased. Flexural strength for the modified resins decreased gradually with increasing TAIC content. Flexural moduli for the modified resins were comparable to or less than that for the PMS-modified Matrimid resin. T_gs for the modified resins were equal to that for the unmodified Matrimid resin. It is noteworthy that the

use of TAIC as a component of the matrix did not lead to the decrease in T_g for the cured resin, although TAIC was incorporated only by the ene reaction. The retention in thermal property would be because of the rigid structure of the trifunctional isocyanurate ring.

Figure 3 shows the mechanical and thermal properties of the modified resins as a function of PMS concentration on 20 eq % TAIC incorporation. The K_{IC} for the modified resins increased with increasing PMS concentration up to 5 wt % addition of the modifier, leveled off, and then decreased abruptly on 7 wt % addition. These fracture behaviors are similar to those in the modification of the Matrimid 5292 system with PMS.[15] On 5 wt % addition of PMS, K_{IC} increased 100% with a moderate decrease of flexural strength, compared to the results for the unmodified Matrimid resins (Table I, entry nos. control A and 08). Flexural strength for the modified resins decreased with increasing PMS concentration. Flexural moduli and T_g were equal or slightly low compared to that for the unmodified resin. These fracture behaviors correspond to morphologies of the modified resins as shown below.

The modification of the Matrimid resin by PMS was reexamined (Fig. 3) as the curing conditions in
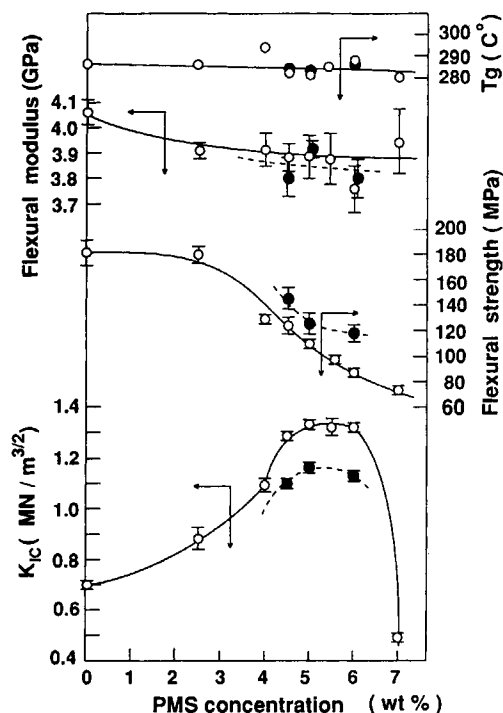

Figure 3 Physical properties for the modified resins as function of PMS concentration in the matrix compositions consisted of DBA and TAIC (80 : 20 eq. ratio) as allyl component (○) with TAIC and (●) without TAIC.
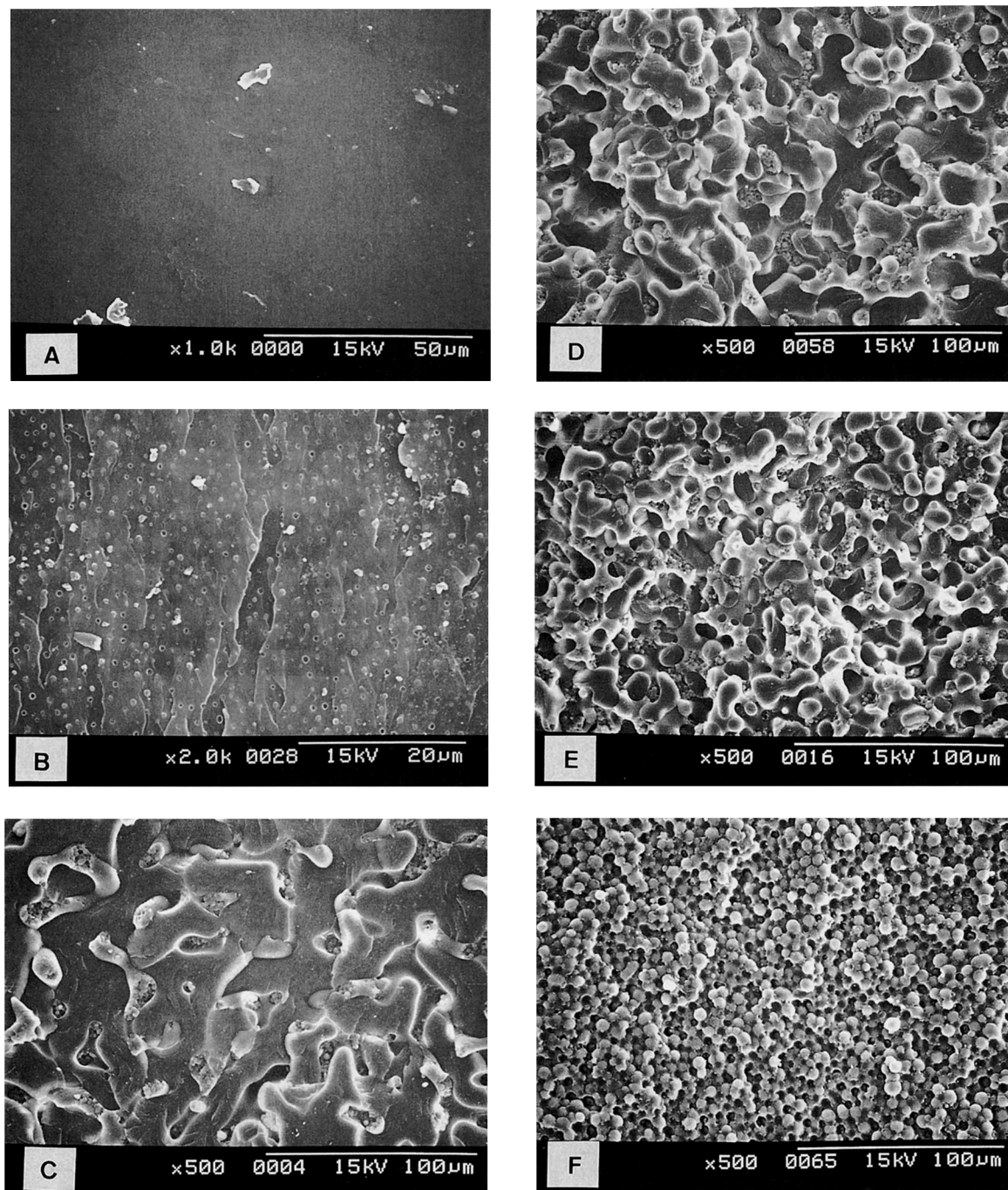
Figure 4   SEMs of fracture surfaces for the cured resins modified in the presence of TAIC 20 eq %. Amount of PMS, in wt %: (A) 0 (control); (B) 2.5; (C) 4.0; (D) 5.0; (E) 6.0; (F) 7.0.

this study were different from those in the previous study,[15] but the K_{IC} values were very similar to each other. The fracture results indicate that PMS became more effective in the use of TAIC as one component of the bismaleimide matrix.

Morphologies of Modified Bismaleimide Resins

The morphologies of the cured resins were investigated by the SEM. Figures 4 and 5 show SEMs for the modified resins. The unmodified cured Matrimid
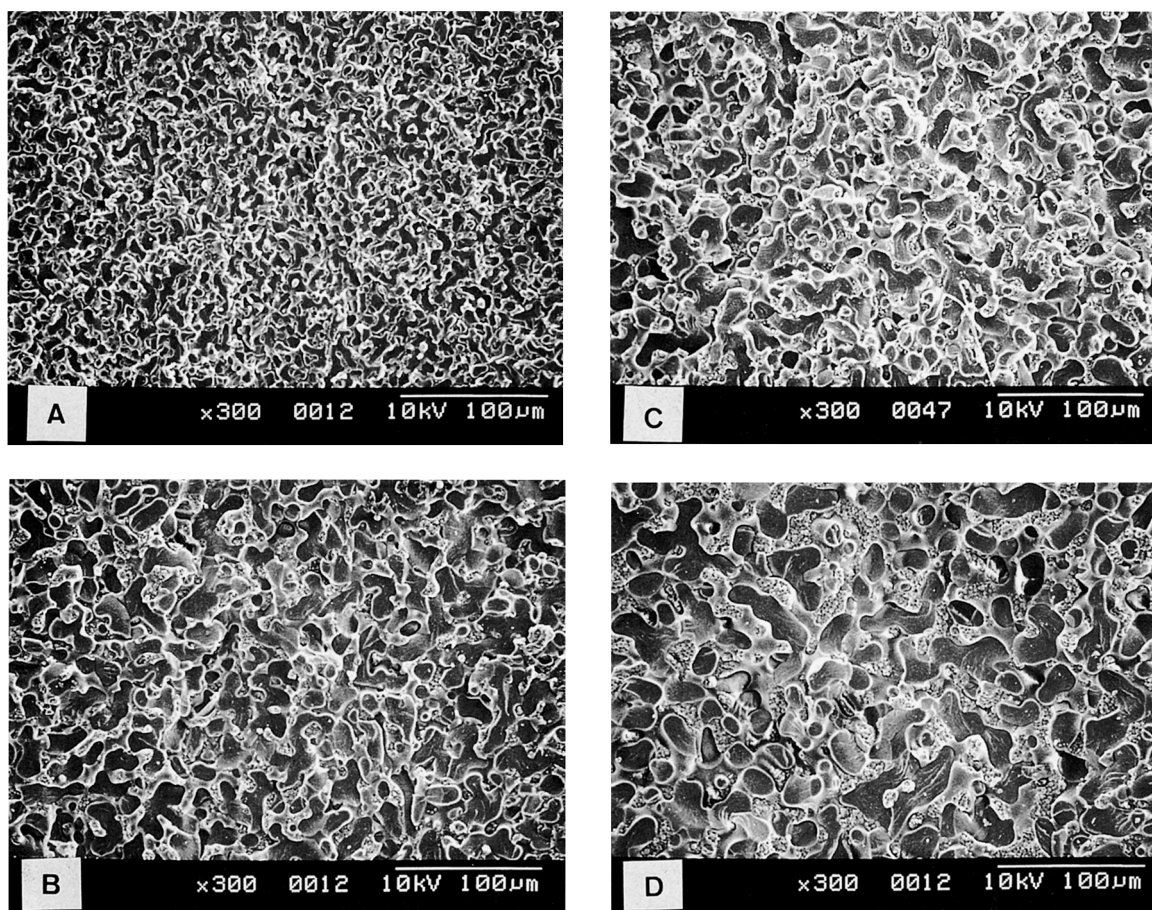
Figure 5 SEMs of fracture surfaces for the cured resins modified with 5 wt % addition of PMS (M_w 303,000). Amount of TAIC, in eq %: (A) 0; (B) 10; (C) 20; (D) 30. The scale bars are 100 μm.

resins had only one phase as reported previously.[15] The cured bismaleimide resin containing TAIC as one of the allyl components was also transparent and had a featureless morphology [Fig. (4A)]. Inclusion of PMS led to two-phase morphology. The morphologies of the modified resins depended drastically on the PMS concentration. When using 2.5 wt % of PMS in the Matrimid matrix system containing 20 eq % of TAIC, the modified resin had a two-phase morphology with PMS-rich spherical particles dispersed in the bismaleimide-rich matrix [Fig. (4B)]; the average diameter of the particle was 0.49 μm and the volume fraction (0.081) of the PMS-rich particles was far larger than the feed weight fraction (0.025) of PMS. In the modification with 4 wt % of PMS, the PMS-rich phase tended to coagulate and form a continuous phase structure, where few larger PMS-rich particles were still observed [Fig. (4C)]. The 5 wt % PMS-modified resin had a cocontinuous phase morphology [Fig. (4D)]. On 6 wt % addition of PMS the morphology of the

modified resin was an intermediate structure from a cocontinuous phase to a phase-inverted structure, and dark flat irregular-shaped bismaleimide-rich domains were observed [Fig. (4E)]. The modified resin had a typical phase-inverted morphology with blending 7 wt % of PMS [Fig. (4F)], for example, the connected global structure reported by Yamanaka and Inoue as the result of the reaction induced phase separation by the spinodal decomposition in the DGEBA/p,p'-diaminodiphenyl methane/PES modification[20]; but the toughening of the bismaleimide resin in the present modification could be attained because of the cocontinuous phase morphology and the phase-inverted structure was undesirable, just as in the modification of the Matrimid resin with PMS.[15]

The dependence of morphology on the matrix compositions was studied on 5 wt % addition of PMS (Fig. 5). The extent of dispersion of cocontinuous phase became lower with increasing TAIC content in the matrix compositions because of lower com-

patibility of PMS with the matrix containing TAIC. When using TAIC as one of the allyl components, the crosslink density of the matrix became larger than the cured Matrimid resin as shown later in dynamic viscoelastic behaviors (Fig. 6). The dispersibility of the PMS-rich continuous phase would be restricted because of the increase in the crosslink density of the matrix. The dispersibility of the cocontinuous phase did not correspond to the improvement in toughness in the present modification. These results indicate that the morphology of the modified resin could be controlled to some extent by blending TAIC, and that there would be an optimum extent of dispersion of the cocontinuous phase to improve the toughness to a greater extent. In the present modification system the matrix containing 20 eq % TAIC is a desirable matrix composition.

The similar relation between the fracture behavior and the morphology of the modified resin could be observed in the modification of epoxies. PMS was effective for both epoxy and bismaleimide (Matrimid 5292) resin modifications.[13-15] To obtain more effective modifiers, reactive PMSH having p-hydroxystyrene (HSt) units reacting with epoxies was used for epoxies.[17] The extent of dispersion of the cocontinuous phase became higher with increasing HSt unit content in PMSH, because the compatibility of PMSH with the epoxy matrix increases with increasing the HSt unit content because of chemical blending. But the K_{IC} values for the modified resins decreased with increasing dispersibility of the

PMSH-rich phases. Then it was thought that there would be an optimum extent of dispersion of the cocontinuous phase to improve the toughness of epoxies in the modification with PMSH.

Dynamic Viscoelastic Analysis of Modified Resins

Dynamic viscoelastic analysis can give information on the microstructure of cured resins. Figure 6 shows the matrix composition dependence of the storage moduli, G', and tan δ curves for the unmodified resins. When using 20 eq % of TAIC as the component of the matrix, the peak position of the α relaxation in the tan δ curve shifted toward higher temperature, its magnitude became smaller, and its shape became broader, compared with dynamic viscoelastic behavior for the cured Matrimid resin. The smaller magnitude of the α relaxation would be because of less mobility of the matrix containing TAIC. The broadness of the α relaxation indicates the complexity of the matrix structure based on TAIC incorporating into the network. The equilibrium storage modulus in the rubber region at higher temperature than the α relaxation corresponds to the crosslink density of the matrix. Despite using TAIC incorporated into the matrix only by the ene reaction, the storage modulus over T_g of the cured resin was larger than the cured Matrimid resin. This is perhaps because of the trifunctional rigid isocyanurate ring structure of TAIC.

In the modification of the bismaleimide resin containing 20 eq % of TAIC with PMS, the α-re-
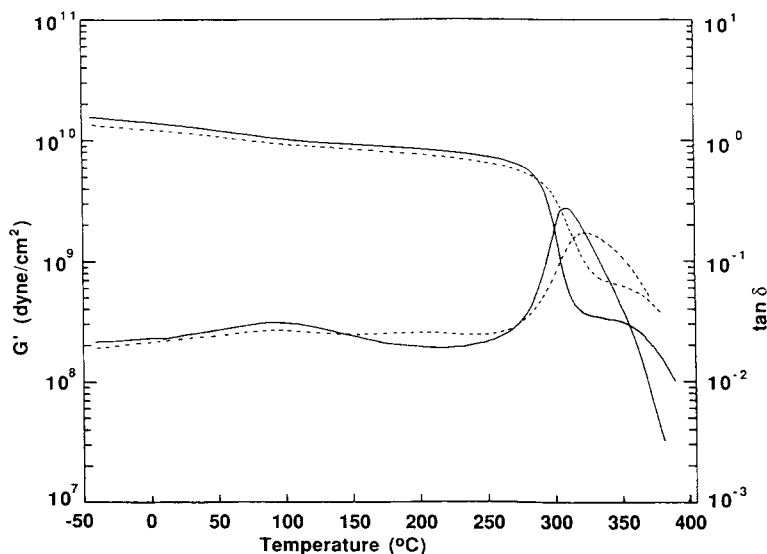

Figure 6   The dependence of dynamic viscoelastic behavior of unmodified resins on the matrix compositions: (—) TAIC 0 eq % (control) and (---) TAIC 20 eq %.
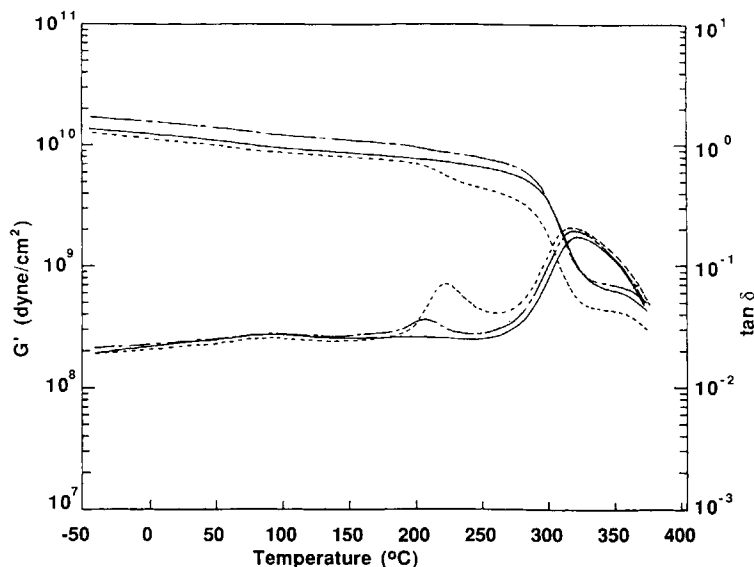
Figure 7 Dynamic viscoelastic analysis for unmodified and PMS-modified resins containing TAIC 20 eq %: (—) 0 wt % (control); (---) 2.5 wt %; (---) 5 wt %.

laxation peak became slightly broader, its position shifted slightly toward lower temperature, and its magnitude became higher, compared to those for the unmodified resin (Fig. 7). A new relaxation peak (α' relaxation) was observed at 207°C on 2.5 wt % addition of PMS. The magnitude of the α' relaxation became larger on 5 wt % addition and its position shifted to 223°C. The appearance of the new α'-relaxation peak in the tan δ curve indicates the existence of the phase-separated structure for the PMS-modified resin. These results correspond to the morphological results. The storage moduli at room temperature for the modified resin were equal or larger compared to that for the unmodified resin. The storage modulus over T_g of the modified resin decreased on 5 wt % addition of PMS.

CONCLUSION

PMS was effective as the modifier for the bismaleimide resin. The improvement in toughness of the PMS-modified bismaleimide resin could be achieved because of the cocontinuous phase morphology to a greater extent when using TAIC as the component of the matrix. The increase in TAIC content resulted in the lower extent of dispersion of the PMS-rich continuous phase, but the efficiency of PMS did not correspond to dispersibility of the PMS-rich continuous phases. It is thought that there would be an

optimum extent of dispersion of the cocontinuous phase to improve the toughness. The most suitable matrix composition for modification of the bismaleimide resin was inclusion of 20 eq % of TAIC, which led to a 100% increase in K_{IC} at moderate loss of flexural strength and with retention in flexural modulus and T_g on 5 wt % addition of PMS (M_w 303,000).

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