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MODIFICATION OF BISMALEIMIDE RESIN BY *N*-PHENYLMALEIMIDE-STYRENE COPOLYMERS

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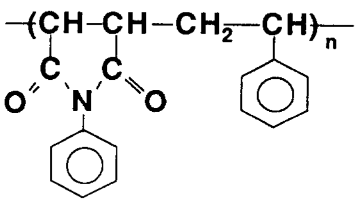
Abstract—*N*-Phenylmaleimide-styrene alternating copolymers were used to improve the toughness of the bismaleimide resin composed of bis(4-maleimidediphenyl) methane and *o,o'*-diallyl bisphenol A. The most suitable composition for modification of the bismaleimide resin was inclusion of 5 wt% of the copolymer (M_w 231,000) which led to a 50% increase in the fracture toughness (K_{IC}) of the cured resin with a medium expense of its flexural strength. The glass transition temperatures of the modified resins were equal to or slightly less than that of the unmodified bismaleimide resin. The modified resins had different phase separation morphologies, depending on the copolymer molecular weight and concentration. The toughening mechanism was discussed in terms of the morphological characteristics of the modified bismaleimide resin systems.

INTRODUCTION

Addition polyimide resins are among 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 were also investigated because of good processability and nonvolatility. Recently a two-component bismaleimide system (Matrimide 5292), composed of bis(4-maleimidediphenyl) methane and *o,o'*-diallyl bisphenol A, has been developed by Chiba Geigy Co. to improve mechanical properties and processability [1]. *o,o'*-Diallyl bisphenol A copolymerizes with bismaleimide via an ene type linear chain extension reaction during curing. Then the toughening in this resin system is based on the decrease in the cross-link density, 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 has been increased by blending with reactive liquid rubbers such as carboxyl-terminated butadiene acrylonitrile rubbers (CTBN) [2, 3] or terminally functionalized engineering thermoplastics [4–7]. Reactive elastomers are rather less effective in the highly cross-linked epoxy [3, 8]. Engineering thermoplastics are suitable for improving the toughness of bismaleimide resins from the viewpoint of the maintenance of mechanical and thermal properties for the matrix resin. Modification of the bismaleimide resin was carried out on the basis of the information on the toughening of epoxies in our laboratory [9–12]. More recently, we have found that poly(*N*-phenylmaleimide-alt-styrene) (PMS) was an effective modifier for the diglycidyl ether of bisphenol-A (DGEBA)/*p,p'*-diaminodiphenyl sulphone (DDS) system [13]. We have also found that PMS was the effective modifier for toughening of the highly cross-linked epoxy matrix such as the triglycidyl aminocresol (TGAC)/DDS system [14]. PMS was prepared by radical copolymerization of *N*-phenylmaleimide and styrene. In spite of the carbon carbon single bond repeating units, PMS has a high transition temperatures of over 200° because of the bulkiness of the two side groups in PMS. Furthermore, the high molecular weight polymer could be easily prepared, whereas it is rather difficult to obtain engineering thermoplastics with high molecular weights, as they are generally prepared by polycondensation. In the previous paper [13] the morphologies of the modified epoxy resins have depended on both PMS molecular weight and concentration and the most effective modification has been attained based on the co-continuous phase structure. This paper reports the modification of the bismaleimide resin (Matrimide 5292) with PMS. The effect of the molecular weight and the amount of PMS added on the toughness of the cured maleimide resin was examined.



EXPERIMENTAL PROCEDURES

Materials

The bismaleimide resins system was a commercial product composed of bis(4-maleimidediphenyl) methane (BMI) and *o,o'*-diallyl bisphenol A (DBA) (Chiba Geigy Co., Matrimide 5292). *N*-Phenylmaleimide (PMI) was provided by Nippon Shokubai Corporation. Styrene (St) was purified in the usual way. PMS was prepared as reported previously [13]. Other reagents were used as received.

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Table 1. Preparation and characterization of PMS*

Entry No.	$C_{12}H_{25}SH$† (mol%)	Yield (%)	M_w‡ (10^4)	M_n‡ (10^4)	M_w/M_n	T_g§ (°C)
1¶	0.35	98	6.7	2.4	2.82	216
2	0.2	87	15.0	6.4	2.35	222
3	0.1	87	23.1	11.1	2.01	221
4	0	90	42.9	20.4	2.09	225

*Feed composition, PMI: St 1:1 mol ratio; in acetone at 60°.

†Chain transfer agent.

‡By GPC.

§By DSC.

¶In benzene at 70°.

Measurements

Molecular weights of copolymers 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. Specimens for flexural measurements are machined with a diamond wheel saw (4 × 10 × 80 cm), while cooling with water, and dried. Flexural tests were carried out at a cross head speed of 2 mm/min (JIS K7203). Rectangular fracture toughness specimens were machined with dimensions of 7 × 14 × 80 cm, a sharp starter crack (*ca* 1.5 mm length) was introduced at the base of the notch (*ca* 5.5 mm length) by a new razor blade tapping, and fracture toughness, K_{IC}, was measured in a three-point bent geometry at a cross head speed of 1 mm/min (ASTM E-399). Glass transition temperature of both PMS and cured resins were measured by differential scanning calorimetry (Shimadzu DSC 41 M type) at a heating speed of 10°/min. Scanning electron micrographs were taken with a Hitachi SEM S-2100A instruments using failed specimens in the K_{IC} tests. Solvent-etching of fracture surfaces was carried out by immersing specimens in tetrahydrofuran (THF) at room temperature for 10 days. Dynamic viscoelastic analysis was performed with a Rheometrics RDS II type (Rheometrics Co.) between room temperature and 350° at a heating speed of 5°/min at frequency of 10 radians/sec.

Curing procedure

PMS was dissolved in DBA without solvents by heating at 160°, Then BMI were added into the mixture, which was kept at 130° for about 40 min to dissolve BMI. DBA and BMI were used in a molar ratio of 1:1. The resulting clean mixture was degassed *in vacuo* and poured into moulds, preheated at 130°, to obtain 4 or 7 mm thick plaques. The mould consisted of one pair of upright and metal crip-held glass plates spaced by U-shaped silicone rubber stick. The amount (wt%) of PMS used was calculated based on the Matrimide 9252 system. The curing cycle was 160°/3 hr + 180°/1 hr + 200°/2 hr + 250°/6 hr. It is noteworthy that the cooling schedule for the cured resins is important in the curing of the bismaleimide resin. After curing, cooling was carried out by decreasing gradually the oven temperature from 250° to room temperature and the time taken to reach 50° was about 5 hr.

RESULTS

Mechanical and thermal properties of modified bismaleimide resins

The copolymerization reactivities of PMI have already been studied and the copolymerization of PMI and styrene gives alternating copolymers, PMS independent of the feed monomer composition [15]. Table 1 reports some characteristic properties of the copolymers. The polymerization in aromatic hydrocarbons such as benzene led to a widening of the molecular weight distribution (M_w/M_n), because aromatic hydrocarbons are rather poor solvents for PMS. The molecular weights of PMS could be controlled by using dodecanethiol as a chain transfer agent. The weight average molecular weight (M_w) was used as a measure of the molecular weight (MW), because the number average molecular weight is highly sensitive to the presence of a small amount of lower molecular weight material. The glass transition temperature (T_g) of PMS increased with increasing molecular weight.

The cured parent bismaleimide resin was transparent, but the modified resins became translucent. Figure 1 shows the PMS (5 wt%) MW dependence of fracture toughness, K_{IC}, for the modified resins. When using PMS with MW < 150,000, the K_{IC} values increased about 10%. The use of PMS with MW > 200,000 led to a considerable increase in K_{IC}. For example, inclusion of 5 wt% of PMS (MW 231,000) resulted in a 50% increase in K_{IC}. Figure 2 shows the PMS (5 wt%) MW dependence of physical properties for the modified resins. The flexural strength for the modified resins decreased with increasing PMS MW. Flexural moduli for the modified resins increased, compared to that for the parent bismaleimide resin. T_gs for the modified resins were equal to or slightly less than that for the parent resin.

Figures 3 and 4 show the mechanical and thermal properties of the PMS-modified resins as a function of concentration of PMS. PMS with MW < 150,000 was less effective as a modifier for the bismaleimide resin. In the modification with higher MW (231,000)

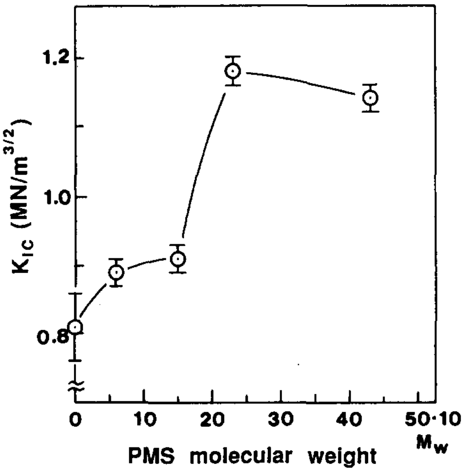

Fig. 1. Dependence of fracture toughness for modified resins on PMS molecular weight. 5 wt% PMS addition.

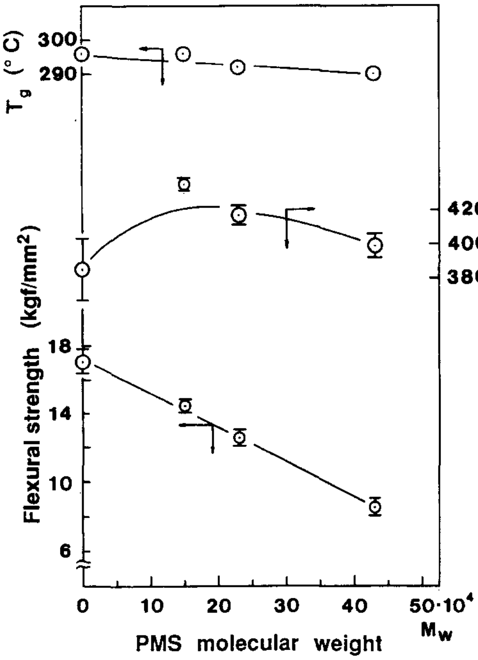

Fig. 2. Dependence of physical properties for modified resins on PMS molecular weight. 5 wt% PMS addition.

PMS, K_{IC} for the modified resin increased on addition of 5 wt% of PMS and then decreased abruptly (Fig. 3). The flexural strength for the modified resin decreased with increasing low MW PMS (150,000) concentration. When using PMS with high MW (231,000), the flexural strength for the modified resins hardly changed on addition of 2.5 wt% of PMS, but decreased on addition of 5 wt% (Fig. 4). Flexural moduli for the modified resins were larger than that for the parent resin. T_gs for the modified resins decreased gradually with increasing PMS concentration. The cured resins could not be prepared because of the high viscosity of the uncured bismaleimide mixtures at 130°, when using 10 wt% of high MW PMS.

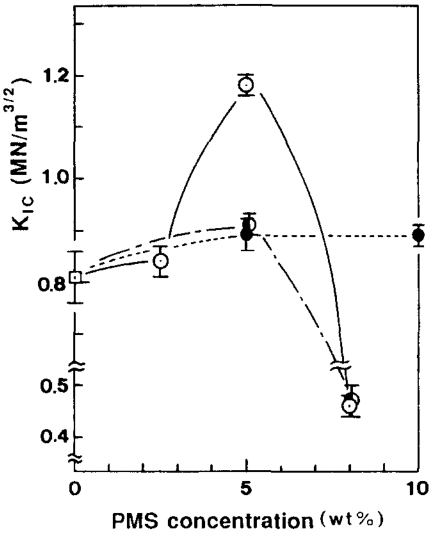

Fig. 3. Fracture toughness of PMS-modified resins as function of PMS concentration. M_w of PMS used: □, control; ●, 67,000; ◐, 150,000; ○, 231,000.

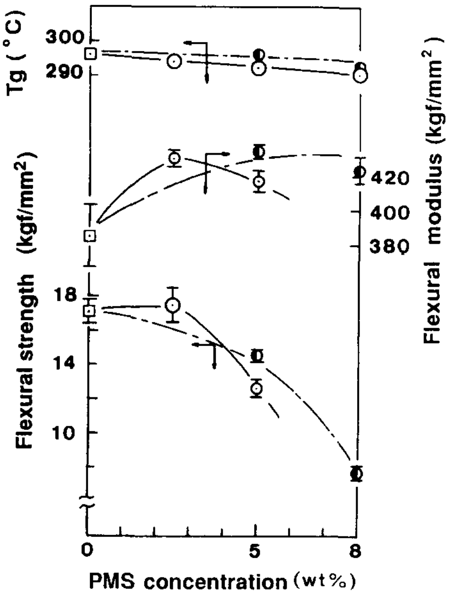

Fig. 4. Physical properties of PMS-modified resins as function of PMS concentration. M_w of PMS used: □, control; ◐, 150,000; ○, 231,000.

Morphologies of modified bismaleimide resins

The morphologies of the cured resins were investigated by the scanning electron micrographs (SEMs). Figure 5 shows SEMs of both the unmodified and PMS (5 wt%)-modified resins. The parent bismaleimide resin had only one phase and the fracture surface was smooth and featureless except for large fracture steps [Fig. 5(A)]. Inclusion of PMS led to phase separation. The morphologies of the cured resins changed drastically, depending on the PMS MW and concentration. When using 5 wt% of PMS with MW 67,000, the modified resin had two phase separation structure; the PMS-rich phase formed somewhat irregular spherical particles (*ca* 0.5 μm in the average diameter, D) dispersed in the bismaleimide-rich matrix, together with the localized plastic deformation caused by the particles at the fracture [Fig. 5(B)]. On addition of 5 wt% of PMS with MW 150,000 the modified resin still had two-phase separation morphology, but the particle size distribution was much broader, large particles (D, *ca* 4.5 μm) were aggregation of small particles, and part of the large particles began to coagulate [Fig. 5(C)]. The morphology of the modified resin became a co-continuous phase structure in modification with high MW PMS (231,000) [Fig. 5(D)]. The PMS-rich phase is a cluster of small particles of PMS. Figure 7 shows a change in morphology with increasing PMS concentration in the modification with high MW PMS (231,000). On addition of 2.5 wt% of PMS the modified resin had two-phase morphology with spherical particles (D, *ca* 0.4 μm) dispersed in the matrix [Fig. 6(A)]. When using 5 wt% of the same

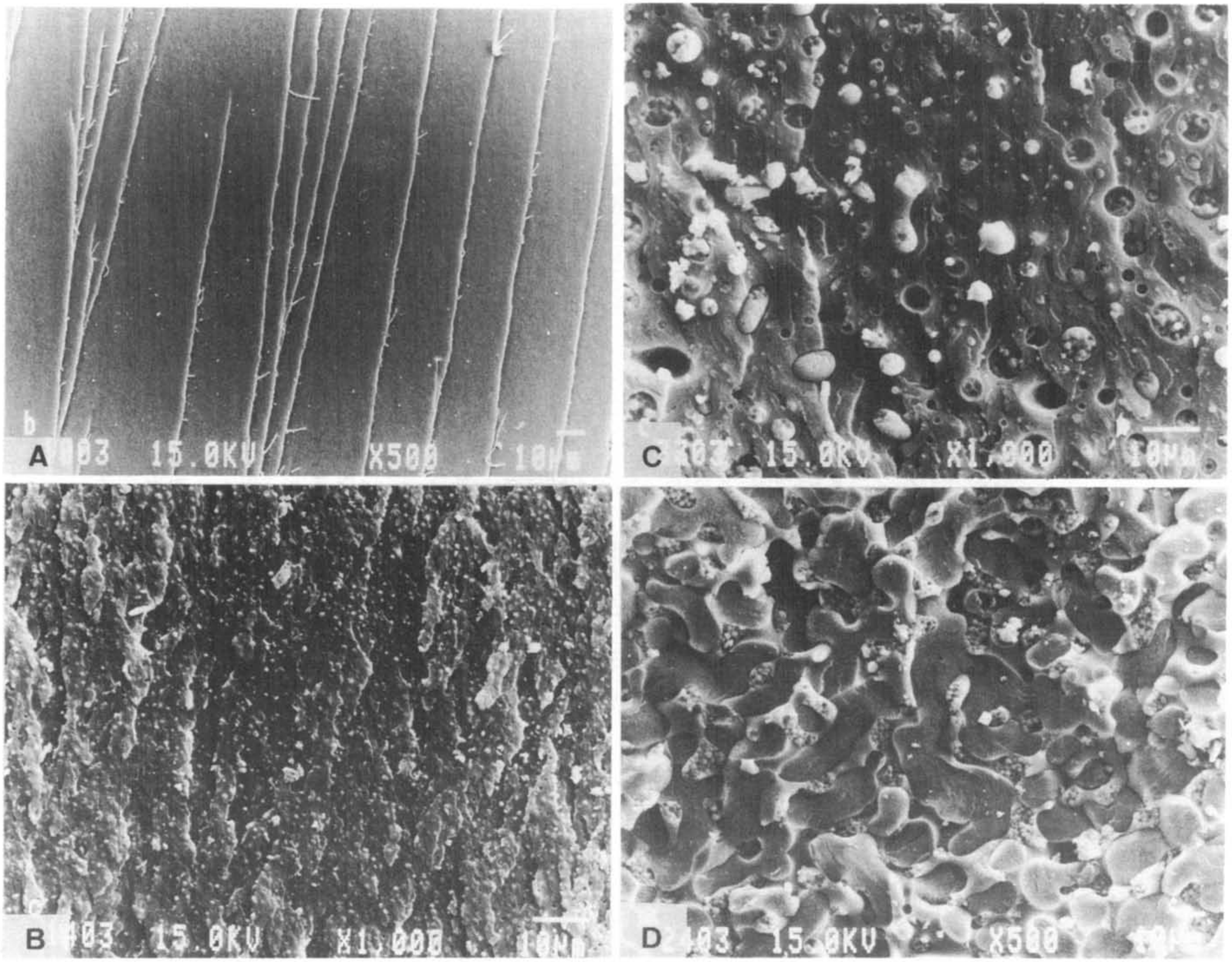

Fig. 5. SEMs of fracture surfaces for the cured resins modified with 5 wt% of PMS. M_w of PMS used: (A) control; (B) 67,000; (C) 150,000; (D) 231,000.

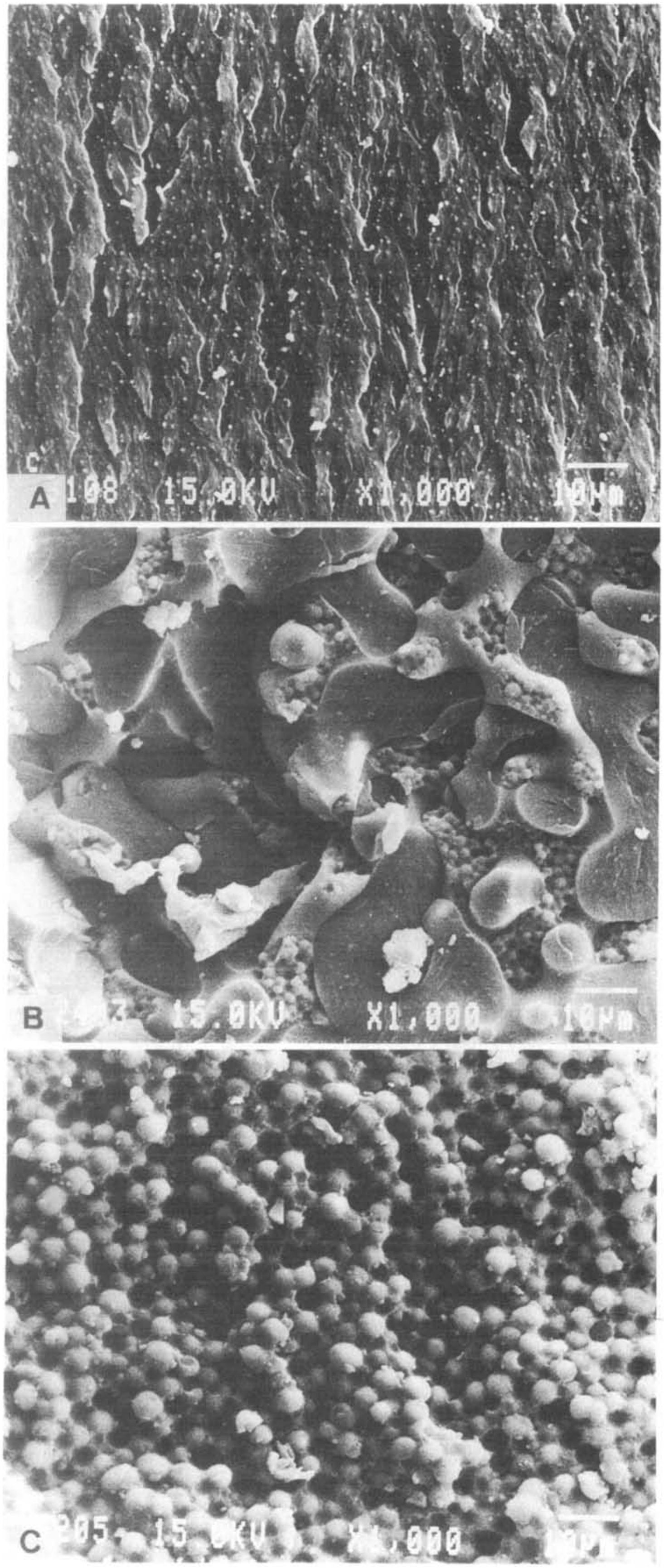

Fig. 6. SEMs of fracture surfaces for the cured resins modified with PMS. Amount of PMS (M_w 231,000): (A) 2.5 wt% addition; (B) 5 wt% addition; (C) 8 wt% addition.

modifier the particles formed continuous phases and the PMS-rich phase was composed of adhesived PMS particles [Fig. 6(B)]. On addition of 8 wt% the morphology of the modified resin further changed and the phase inversion was observed [Fig. 6(C)], where parts of the torn PMS-rich phase adhered on the epoxy-rich particle surfaces as shown in etching of fracture surfaces below.

Solvent-etched fracture surfaces were also taken by SEMs to examine the interfacial adhesion between the PMS-rich phase and the bismaleimide matrix. Etching was carried out in THF at room temperature for 10 days, but part of the PMS-phase still remained [Fig. 7(A)]. The fracture surfaces of the modified resin with the phase inversion morphology became clear by etching [Fig. 7(B)], compared to the unetched fracture surface [Fig. 6(C)]. These morphological results indicate that the particles, observed in Fig. 6(C), are bismaleimide-rich and the PMS-rich phase is incorporated between the particles.

Dynamic viscoelastic analysis of modified bismaleimide resins

Dynamic viscoelastic analysis can give information on the micro-structure of cured resins. Figure 8 shows the storage moduli, G', and tan δ for the unmodified and PMS (M_w 231,000)-modified resins. The peak position of the α-relaxation in the tan δ curves shifted toward lower temperature in the modification with PMS, and the peak became broader, compared with the dynamic viscoelastic behaviour for the parent bismaleimide resin. Further, an α'-relaxation peak appeared at *ca* 230° on addition of 2.5 wt% of PMS and became larger with increasing PMS concentration (5 wt%). The storage moduli in the glass state were equal or larger compared to the unmodified resin. The PMS (8 wt%)-modified resin failed during measuring, perhaps because of its poor mechanical strength.

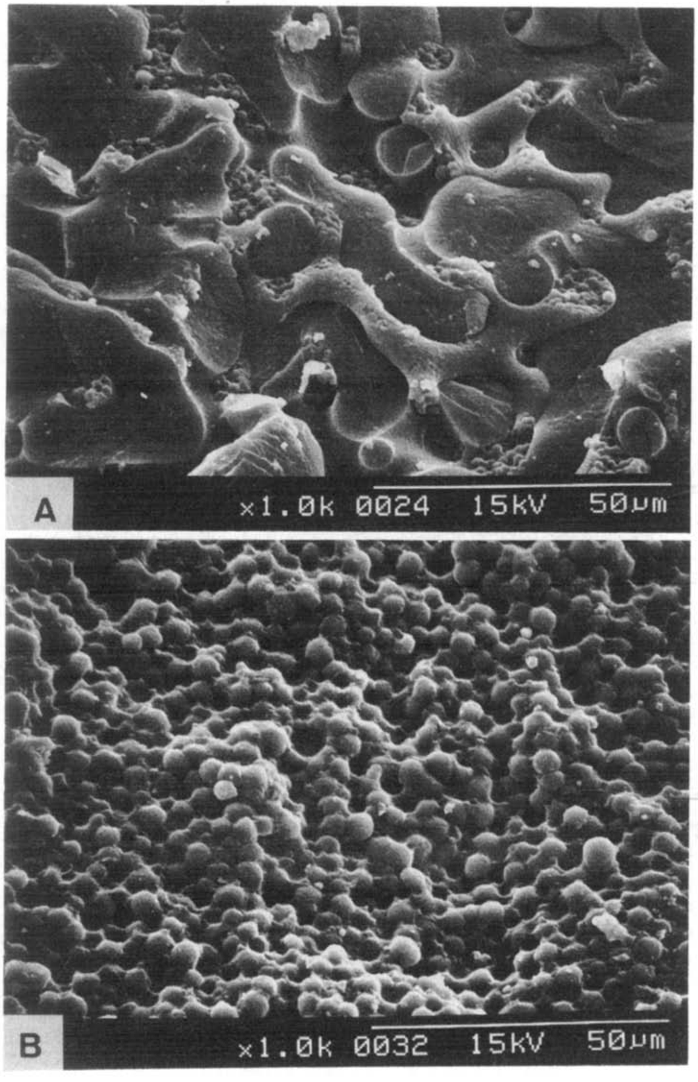

Fig. 7. SEMs of fracture surfaces for the cured resins modified with PMS, etched with THF. Amount of PMS (M_w 231,000): (A) 5 wt% addition; (B) 8 wt% addition.

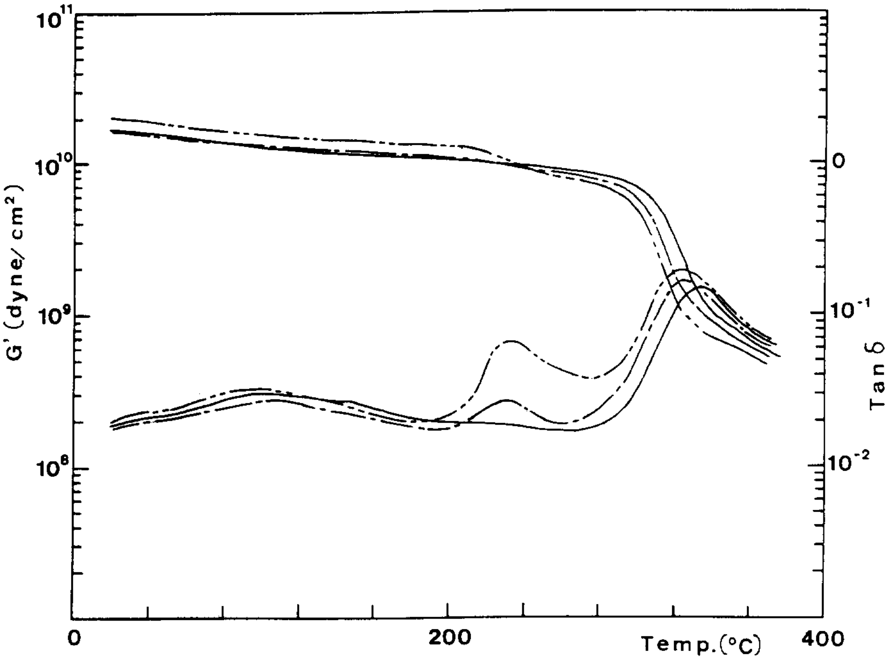

Fig. 8. Dynamic viscoelastic analysis for unmodified and PMS-modified resins. PMS, M_w 231,000; ——, control; — - —, 2.5 wt% addition; — - - —, 5 wt% addition.

DISCUSSION

PMS was an effective modifier for improving the toughness of the bismaleimide resin, but fractural behaviour was complicated depending on both PMS MW and concentration. The use of PMS (5 wt%) with MW < 150,000 led to a slight increase in K_{IC} and the modified resins had two-phase morphologies. When using higher MW PMS (231,000), K_{IC} for the modified resin increased 50% with a medium expense of its flexural strength (Figs 1 and 2). In the modification with PMS of MW 231,000, K_{IC} increased discontinuously with increasing PMS concentration and then decreased abruptly (Fig. 3), together with the change in morphology. The flexural strength for the modified resins decreased with increasing PMS MW and concentration perhaps because of insufficient interfacial adhesion between the matrix and the modifier, based on physical interactions such as the van der Waals forces, but the flexural modulus increased and T_g decreased slightly on modification (Figs 2 and 4).

The morphological behaviour of the modified resins is interesting and instructive when considering the toughening mechanism in the present modification systems. Inclusion of 5 wt% of PMS led to drastic change in the morphology of the modified resins, depending on PMS MW. When using PMS of MW 67,000, two-phase morphologies were observed [Fig. 5(B)]. In the modification with PMS of MW 150,000, the PMS particles became larger and began to coagulate [Fig. 5(C)]. On addition of higher MW PMS (231,000) the modified resin had the co-continuous phase morphology [Fig. 5(D)]. These morphological behaviours correspond to the dependence of K_{IC} on PMS MW (Fig. 1). K_{IC} for the modified bismaleimide resin increased based on the co-continuous phase structure. The PMS concentration dependence of the morphological behaviour was investigated on the modification with the most effective modifier (MW 231,000) (Fig. 6). Even in the use of higher MW PMS, the modified resin had the two phase morphology on addition of 2.5 wt% of the modifier. On addition of 5 wt% of PMS the PMS-rich particles coagulated and formed the co-continuous phase, together with the increase in K_{IC} (Fig.3). When using 8 wt% of PMS the phase inversion occurred and K_{IC} decreased abruptly. The fractural result on 8 wt% addition is quite unexpected, considering that K_{IC} for the modified resins increased with the phase inversion morphology in the modification of epoxies with poly(etherimide)s (PEI) [16], where a phase inversion was observed on addition of 20 wt% of PEI on the modification of dicyandiamide-cured epoxy (TGAC) resin. In the present modification the phase inversion occurred on only 8 wt% PMS concentration. Such PMS concentration might be too small for toughening of the modified resin, because the PMS-rich phase was incorporated between the bismaleimide-rich particles, formed the continuous phase and absorbed fracture energy due to ductile drawing and tearing at fracture. SEMs before and after etching show the extent of interfacial adhesion between PMS and the matrix. The PMS-rich continuous phase in the modified bismaleimide resins could not be removed clearly by etching with THF for 10 days (Fig. 7). On the other hand, the PMS-rich continuous phase in the modified DGEBA epoxy resins were removed clearly by etching with THF for 2 days and irregular deep holes remained as reported previously [13], which fact indicates that there is no chemical interfacial adhesion between the epoxy matrix and PMS. The morphologies after etching indicate that the physical interaction of the bismaleimide matrix and PMS is stronger than that of the DGEBA epoxy matrix and PMS. In spite of rather strong physical adhesion, the flexural strength for the PMS-modified resins decreased. It is thought that such deficiency would be overcome by introducing functional groups into the modifier.

The appearance of the α'-relaxation peak at *ca* 230° in the tan δ curve indicates the presence of phase-separation for the modified resins. Dynamic viscoelastic behaviour corresponds to the morphology of the cured resin. The storage modulus in the plateau region over the α-relaxation temperature in the tan δ curve is related to the cross-link density of the cured resins [8]. The equilibrium storage modulus in the rubber region over the α-relaxation temperature could not be observed and the cross-link density could not be obtained, but the decrease in the storage modulus indicates that the cross-link density would decrease slightly by the modification with PMS (Fig. 8) and so does the decrease in T_g also (Fig. 4).

Fractural behaviour corresponds to the morphology of the modified resins. In every case of this study the toughness of bismaleimide resin could be achieved because of the cocontinuous structure of the modified resins. These results suggest that two toughening mechanisms could operate in the present modification system; one mechanism is owing to two phase separation structure and similar to that in the rubber-modification systems [2, 3] and the other mechanism based on the cocontinuous phase morphology. The contribution to toughening by the former mechanism is not important. Toughening could be attained by the absorption of fracture energy due to ductile drawing and tearing of the PMS-rich co-continuous phase, based on the latter mechanism. This toughening mechanism would be similar to that in the modification of epoxies with engineering thermoplastics such as poly(etherimide)s [6, 7, 16] and poly(ether ketone)s [17]. In the modification of tetraglycigyl-4,4′-diaminodiphenyl methane with poly(etherimide)s (Ultem 1000, GE) (PEI), morphologies of the modified resins changed with increasing PEI content and the toughening of epoxies could be attained by the PEI-rich continuous phase. We have also found that poly(phthaloyl diphenyl ether)s (PPDE) were effective modifiers for DGEBA resins cured with methyl hexahydrophthalic anhydride and that the cocontinuous structure due to the spinodal decomposition was formed in the modified resin with PPDE of higher MW (M_{GPC} 56,300), together with a significant increase in K_{IC} [17].

Engineering thermoplastics have high T_gs because of their rigid structures. PMS has also high T_g owing to the retardation of molecular motion of the main chains caused by the bulky side chains. A drawback in the use of the conventional engineering thermoplastics as modifiers is poor processability, mainly caused by poor compatibility with the uncured bismaleimide resin; in general, the use of a small amount of solvent is essential to dissolve the thermoplastics into the uncured resin on the modification. All of PMS used in this study is soluble in DBA without using solvent. The effectiveness of PMS as modifier could be explained by its similar structure to PEI, where the polar imide units in PEI and PMS would play an important role in the physical interfacial adhesion between the bismaleimide or epoxy matrices and the modifiers.

The T_g values for the resins modified with PMS are equal to or slightly less than that for the unmodified bismaleimide resin.

In conclusion, PMS is an interesting and effective modifier for improving the toughness of bismaleimide resins. Two toughening mechanisms operate in the present modification system depending on PMS MW and concentration; one mechanism is due to two phase separation structure and the other mechanism to the co-continuous phase morphology. The most effective modification for the cured bismaleimide resin can be attained by the latter phase structure. The most suitable composition for modification of the bismaleimide resin was inclusion of 5 wt% of PMS with M_w 231,000. The drawback in the present modification system is the medium decrease in the flexural strength. It is thought that the efficiency of the modifier would increase by enhancing interfacial adhesion due to chemical bonding.

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