Eur. Polym. J. Vol. 28, No. 12, pp. 1539–1545, 1992
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0014-3057/92 \$5.00 + 0.00

TOUGHENING OF EPOXY RESINS BY *N*-PHENYLMALEIMIDE–STYRENE COPOLYMERS

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(Received 13 April 1992)

Abstract—*N*-Phenylmaleimide (PMI)–styrene (St) alternating copolymers were used to improve the toughness of bisphenol-A diglycidyl ether epoxy resin cured with *p,p'*-diaminodiphenyl sulphone (DDS). The most suitable composition for the modification was inclusion of 10 wt% of the copolymer ($\bar{M}_w$ 345,000) which led to a 130% increase in the fracture toughness (K_{IC}) of the cured resin with a medium decrease of its mechanical properties. The glass transition temperatures of the modified resins were equal to or higher than that of the parent epoxy resin. The morphologies of the modified resins were dependent on the copolymer molecular weight and concentration. On addition of up to 7 wt% of the copolymer ($\bar{M}_w$ 345,000) the modified resins had two-phase morphologies with the copolymer-rich dispersed particles in the epoxy matrix. On addition of 8 wt% of the copolymer, the morphologies of the cured resins changed drastically and showed a tendency to form co-continuous phases. The toughening mechanism is discussed in terms of the morphological characteristics of the modified epoxy resin systems.

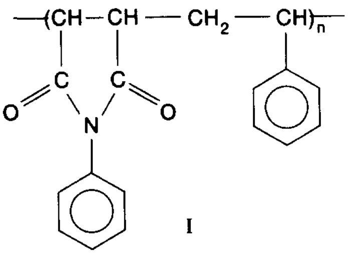
INTRODUCTION

Epoxy resins are some of the most important thermosetting polymers and have wide use as structural adhesives and matrix resins for fibre composites but their cured resins have a 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] or terminally functionalized engineering thermoplastics [2, 3]. In previous papers, various kinds of epoxide-containing acrylic rubbers have been reported as improving the toughness of *p,p'*-diaminodiphenyl sulphone (DDS)-cured epoxy resins, where vinylbenzyl glycidyl ether and glycidyl (meth)acrylates were used as epoxy containing monomers [4–8].

Most of modification with reactive elastomers have been carried out using bifunctional epoxy resins such as diglycidyl ether of bisphenol-A (DGEBA). In the modification of highly cross-inked epoxy matrix, reactive rubbers such as CTBN have been reported as ineffective modifiers [9]. It has also been reported that the reactive acrylic elastomers, butyl acrylate (BA)–glycidyl methacrylate (GMA)–acrylonitrile (AN) terpolymers, are effective in the modification of DGEBA but less effective in the highly cross-linked epoxy matrix formed from triglycidyl aminocresol [8].

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. Modifications of epoxy resins with various types of ductile thermoplastics have been studied as alternatives to reactive rubber toughening for improving the toughness of epoxy resins. At first, commercial poly(ether sulphone)s such as Vitrex were used for modification of polyfunctional epoxies such as tetraglycigyl-4,4'-diaminodiphenyl methane (TGDDM), but were less effective because of high cross-linking structure and poor interfacial bonding between two uncompatibilized phase in the cured resin [10–12]. Terminally functionalized polysulphones are more effective modifiers than commercial PES [2, 13]. Other engineering plastics have also been examined as modifiers; poly(etherimide)s [3, 14–16], poly(aryl ether ketone)s [17, 18] and poly(phenylene oxide) [19] have been reported as effective modifiers. Aromatic polyesters, prepared by the reaction of (iso)phthalic acids and α, ω-alkanediols, were also effective modifiers [20].

During our study of modification of epoxies, we have found that poly(*N*-phenylmaleimide-alt-styrene) (PMS) **I** was an effective modifier; it 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 temperature of over 200°. It is thought that the bulkiness of the two side groups in PMS prevents the molecular motion of the main chain, so raising the



I

Scheme 1

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glass transition temperature. 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. This paper reports the modification of DDS-cured epoxy resins with poly(*N*-phenylmaleimide-alt-styrene). The effects of the molecular weight and the amount of PMS added on the toughness of the cured epoxy resin were examined.

EXPERIMENTAL PROCEDURES

Materials

The epoxy resin was the liquid bisphenol-A diglycidyl ether (DGEBA) [Epikote 828, Shell Chemical Industrial Co., epoxy equivalent weight (EEW) 190]. *p,p'*-Diaminodiphenyl sulphone (DDS) was used as curing agent. *N*-Phenylmaleimide (PMI) was a commercial product (Nippon Shokubai Co.). Styrene (St) was purified in the usual way. Other reagents were used as received.

Measurements

^{1}H-NMR spectra were recorded on a 90 MHz instrument (JEOL JNM-9MX 90) using $CDCl_3$ as solvent and tetramethylsilane as internal standard. 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. Flexural tests were carried out at a cross head speed of 2 mm/min (JIS K7203). 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 temperatures of elastomers 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 JEOL JSM 35 or 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 48 hr. Dynamic viscoelastic analysis was performed with a Rheometrics RDS-II type (Rheometrics Co.) between −150°–250° at a heating speed of 5°/min at frequency of 1 Hz.

Preparation of poly(N-phenylmaleimide-alt-styrene)

The copolymers were prepared from a 1 : 1 mol feed of momomers. The molecular weight of PMS was controlled using dodecanethiol as a chain transfer agent. A typical procedure was as follows:

A flask was charged with PMI (52.0 g, 0.30 mol), St (31.2 g, 0.30 mol), acetone (600 ml), azobisisobutyronitrile (AIBN, 0.99 g, 1 mol%) and dodecanethiol (0.10 g, 0.08 mol%). The flask was purged with N_2 for 0.5 hr and a N_2 atmosphere was maintained through the polymerization. The polymerization mixture was stirred at 60° for 3 hr. After the polymerization was over, the polymerization mixtures were diluted with THF. Then the copolymers were isolated using methanol as precipitant and purified twice by reprecipitation with THF/methanol. The white solid polymers were dried *in vacuo* at 60° and obtained in quantitative yield. The copolymer compositions were determined by elemental analysis.

Curing procedure

The copolymer was dissolved in the epoxy resin without solvents by heating at 140° or 160°, depending on the molecular weight of PMS. Then the curing agent, DDS, was added to the mixture, which was kept at 120° for about 1 hr to dissolve DDS. The resulting clean mixture was poured into a *silicone* mould preheated at 100°. The curing cycle was 120°/1 hr then 180°/5 hr. The curing agent was used stoichiometrically to the epoxy resin. The amount (wt%) of PMS used was based on the epoxy resin, DGEBA.

RESULTS

Characterization of copolymers

The copolymerization reactivities of *N*-phenylmaleimide have already been studied and the copolymerization of PMI and styrene gives alternating copolymers, poly(*N*-phenylmaleimide-alt-styrene) (PMS) I, independent of the feed monomer composition [21]. Table 1 reports some characteristic properties of the copolymers. Polymerization in aromatic hydrocarbons such as benzene led to a widening of the molecular weight distribution ($\bar{M}_w/\bar{M}_n$), because aromatic hydrocarbons are rather poor solvents for PMS. The molecular weights of the copolymers could be controlled by using dodecanethiol as chain transfer agent. The weight average molecular weight ($\bar{M}_w$) was used as a measure of the molecular weight, because the number-average molecular weight is highly sensitive to the presence of a small amount of low molecular weight material. The dependence of physical properties of modified resins on the molecular weight (MW) can be discussed by using $\bar{M}_w$, independent of the molecular weight distribution, as shown later. The glass transition temperature of PMS increased with increasing molecular weight.

Table 1. Characterization of *N*-phenylmaleimide-alt-styrene copolymer (PMS)[a]

Entry No.	$C_{12}H_{25}SH$[b] (mol%)	Yield (%)	Copolymer composition PMI	St	$\bar{M}_w^c$ (10^4)	$\bar{M}_n^c$ (10^4)	$\bar{M}_w/\bar{M}_n$	T_g^d (°C)
1[e]	0	87	54	46	73.4	22.7	3.23	223
2[e]	0	98	51	49	34.4	10.0	3.45	219
3[f]	0	96	—	—	25.8	6.1	4.24	215
4	0.08	94	—	—	23.1	11.5	2.01	223
5	0.2	87	—	—	15.0	6.4	2.34	222
6[g]	1.0	98	—	—	3.6	1.3	2.67	201

[a] Feed composition, PMI:St 1 : 1 mol ratio; in acetone at 60°.
[b] Chain transfer agent.
[c] By GPC.
[d] By DSC.
[e] In benzene.
[f] In toulene at 70°.
[g] In benzene at 70°.

Table 2. Physical properties of cured epoxy resins

PMS[a] Entry No.	Content (wt%)	K_{IC}^{b} (MN · m$^{2/3}$)	n[c]	Flexural properties (kgf/mm^2)[b] Strength	Modulus	n[c]	T_g^d (°C)
	0	0.70 ± 0.05	5	13.8 ± 0.4	351 ± 15	5	180
6	5	0.90 ± 0.04	6	14.8 ± 0.1	300 ± 14	5	183
6	10	0.93 ± 0.02	6	14.7 ± 1.1	300 ± 8	6	183
3	5	0.94 ± 0.03	6	16.5 ± 0.3	325 ± 11	6	183
3	10	1.53 ± 0.04	6	10.0 ± 0.7	329 ± 7	4	183
2	5	1.08 ± 0.06	4	15.5 ± 1.1	314 ± 7	6	183
2	10	1.64 ± 0.07	4	10.2 ± 0.2	328 ± 13	5	183
1	5	0.91 ± 0.05	7	16.6 ± 0.4	340 ± 5	7	187
1	10	1.37 ± 0.06	8	10.5 ± 0.6	336 ± 10	4	188

[a] Entry number in Table 1.
[b] The ± x values show SD.
[c] Specimen number.
[d] By DSC.

Mechanical and thermal properties of modified epoxy resins

Table 2 shows typical results for the modification of the epoxy resin with PMS. The cured parent epoxy resin was transparent but the modified resins became translucent. In the modification with lower molecular weight (MW) PMS ($\bar{M}_w$ 36,000), K_{IC} increased 30% with no loss of mechanical and thermal properties of the modified resin on addition of 5–10 wt% of PMS. The use of higher MW PMS led to a significant increase in K_{IC}. The PMS MW dependence of K_{IC} for the modified resins was investigated in detail (Fig. 1). On addition of 5 wt% PMS, K_{IC} increased 20–30%, independent of PMS MW. When using PMS (10 wt%) with $\bar{M}_w < 150{,}000$, the K_{IC} values increased 30%. The use of PMS (10 wt%) with $\bar{M}_w > 200{,}000$ brought about a significant increase in K_{IC}, together with decreasing flexural strength. For example, inclusion of 10 wt% of PMS ($\bar{M}_w$ 345,000) resulted in a 130% increase in K_{IC}. Flexural moduli for the modified resins decreased slightly, compared to that for the parent epoxy resin. The glass transition temperatures, T_gs, for the modified resins were equal to or higher than that for the parent epoxy resin (Table 2).

Figures 2 and 3 show the mechanical and thermal properties of the PMS-modified resins as a function of concentration of PMS. The K_{IC} values for the modified resins increased gradually on addition of lower MW PMS. In the modification with higher MW PMS, the increased PMS concentration led to a great increase in K_{IC} (Fig. 2). The flexural strength for the modified resins did not decrease even on 10 wt% addition when using PMS with lower $\bar{M}_w$ (36,000). In the use of PMS with high $\bar{M}_w$ (344,000), the flexural strength for the modified resins hardly changed on addition of 5–7 wt% but decreased abruptly in the modification with 10 wt% of PMS. Flexural moduli for the modified resins decreased slightly compared to that for the parent resin. T_gs for the modified resins hardly changed, independent of PMS MW and concentration.

It is noteworthy that PMS with the highest $\bar{M}_w$ (734,000) is somewhat difficult to handle because of an increase in the viscosity of the uncured epoxy mixture.

Morphologies of modified epoxy resins

The morphologies of the cured resins were investigated by scanning electron micrographs (SEMs). The parent epoxy resins had only one phase as reported previously [4]. Inclusion of PMS led to phase separation. The morphologies of the cured resins changed drastically, depending on the PMS MW and concentration. Figure 4 shows SEMs of the cured resins modified with 10 wt% of various samples of PMS. The use of PMS with $\bar{M}_w < 150{,}000$ led to two phase morphology with PMS-rich spherical particles dispersed in the epoxy-rich matrix. The volume fraction

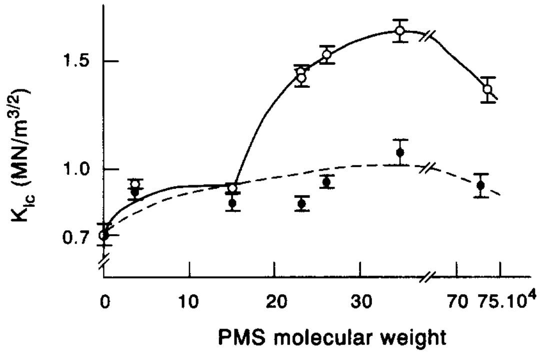

Fig. 1. Dependence of fracture toughness for modified resins on PMS molecular weight. ●, 5 wt% addition; ○, 10 wt% addition.

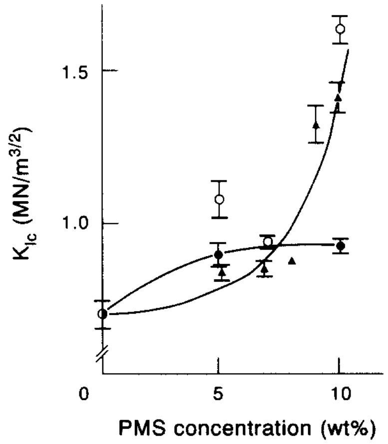

Fig. 2. Fracture toughness for modified resins as function of PMS concentration. ○, $\bar{M}_w$, 344,000; ▲, $\bar{M}_w$, 231,000; ●, $\bar{M}_w$, 36,000.

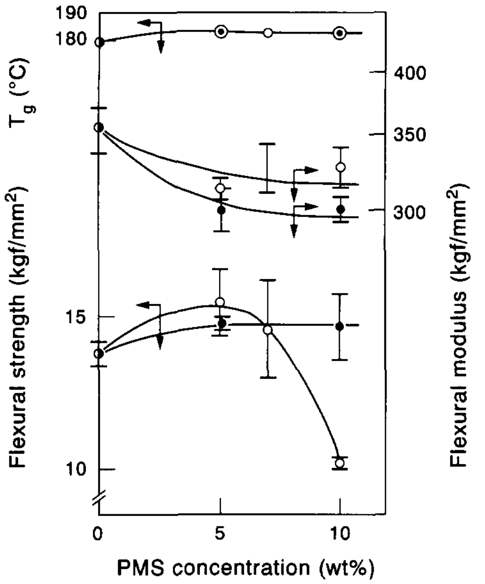

Fig. 3. Physical properties of PMS-modified resins as function of PMS concentration. ○, $\bar{M}_w$, 344,000; ●, $\bar{M}_w$, 36,000.

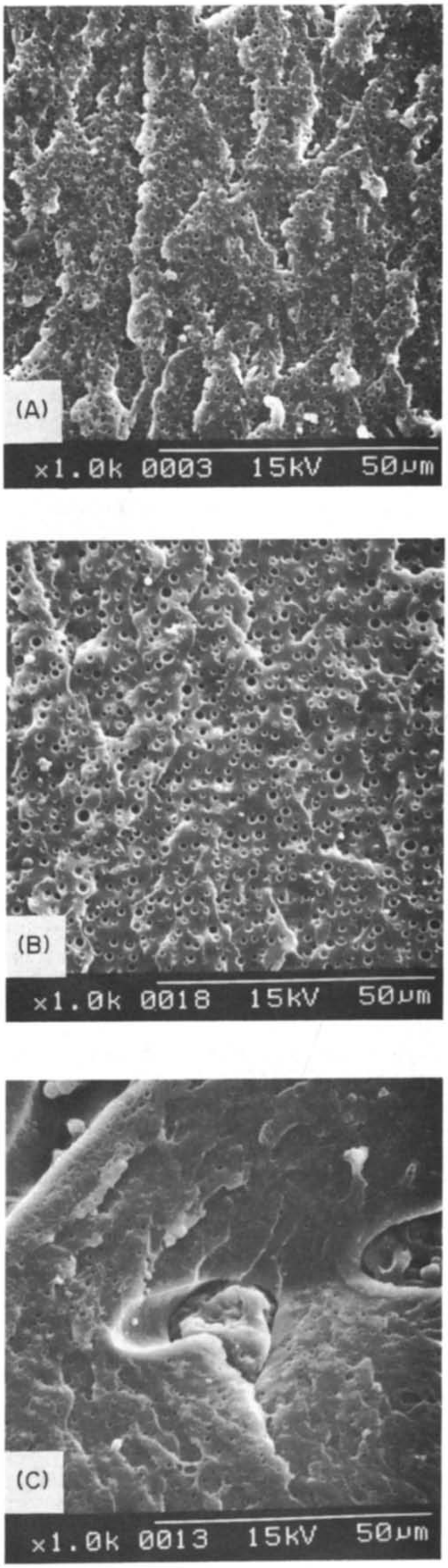

Fig. 4. SEMs of fracture surfaces for the cured resins modified with 10 wt% of PMS. $\bar{M}_w$ of PMS: (A) 36,000 (B) 150,000, (C) 231,000.

(V_f) and the average diameter (D) of the particles increased with increasing PMS MW; V_f and D are 0.16 and 0.67 μm for the PMS ($\bar{M}_w$ 36,000)-modified resin, and 0.25 and 1.13 μm for the PMS ($\bar{M}_w$ 150,000)-modified material, respectively [Figs 4(A) and (B)]. On addition of 10 wt% of PMS with $\bar{M}_w$ 231,000, morphologies changed drastically and the modified resin had a co-continuous phase morphology. Figure 5 shows a change in morphological behaviour with increasing PMS concentration in the modification with high MW PMS. On addition up to 7 wt% of PMS ($\bar{M}_w$ 344,000), the modified resin had two-phase morphology with spherical particles dispersed in the matrix, where V_f and D are 0.16 and 1.06 μm, respectively. When using 8 wt% of the same modifier, the particles began to coagulate and form continuous phase but a small amount of particles remained in the matrix. The amount of particles dispersed in the epoxy matrix decreased with increasing PMS concentration.

Solvent-etched fracture surfaces were also taken by SEMs to examine the interfacial adhesion between the PMS-rich phase and the epoxy matrix. The PMS-phase was removed by etching with THF (Fig. 6). In the two-phase morphologies, the dispersed PMS-rich particles were clearly removed [Fig. 6(A)]. In the co-continuous morphologies, irregular deep holes were observed [Fig. 6(B)]. It is thought that the light phase is PMS-rich, and the dark phase is epoxy-rich in Figs 4 and 5, considering solvent-etched fracture surfaces of the modified resins.

Dynamic viscoelastic analysis of modified epoxy resins

Dynamic viscoelastic analysis can give information on the micro-structure of cured resins. Figure 7 shows the storage moduli, G', and tan δ for the unmodified and PMS($\bar{M}_w$ 344,000)-modified resins. The peak position of the α-relaxation in the tan δ curves hardly changed during modification with PMS but the peak

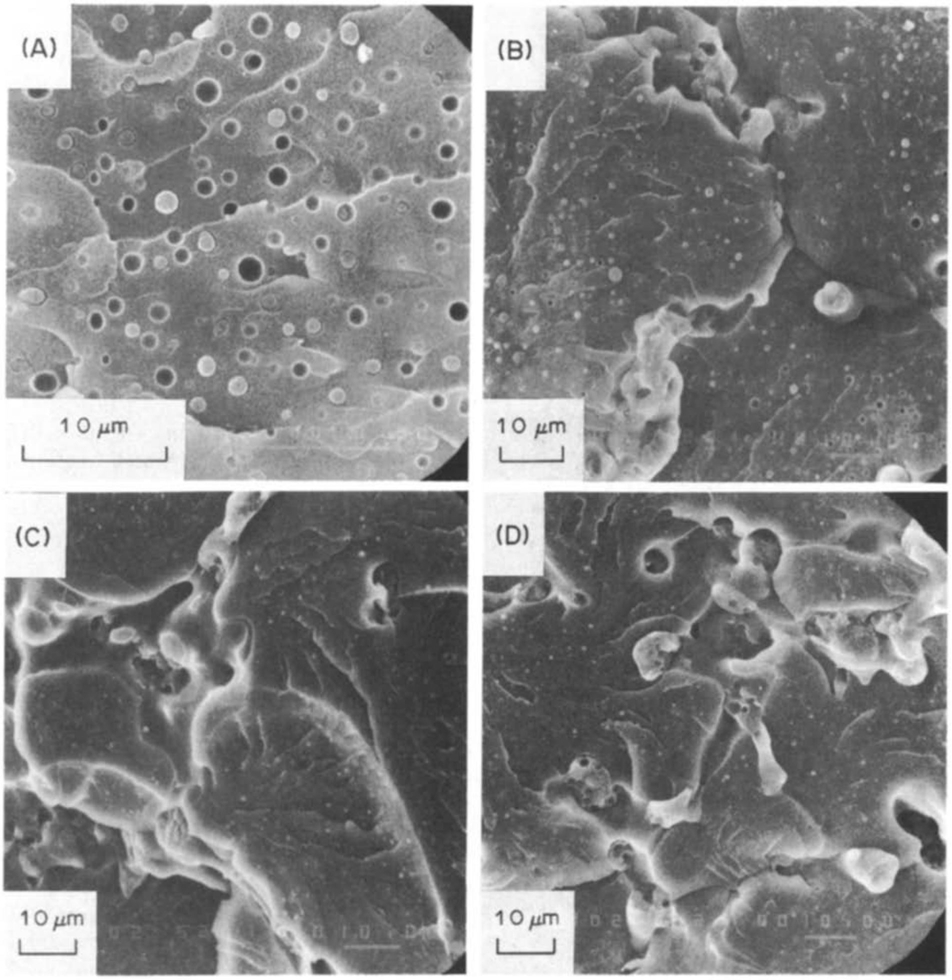

Fig. 5. SEMs of fracture surfaces for the cured resins modified with PMS. Amount of PMS ($\bar{M}_w$ 344,000): A, 7 wt% addition; B, 8 wt% addition; C, 9 wt% addition; D, 10 wt% addition.

became broader on addition of 10 wt% of PMS, compared with the dynamic viscoelastic behaviour for the parent epoxy resin. Further, a shoulder appeared at *ca* 175° on addition of 5 wt% of PMS and shifted to *ca* 185° with increasing PMS concentration (10 wt%). The storage moduli in the glassy state were equal or larger compared to the unmodified resin.

Discussion

PMS was effective for improving the toughness of the epoxy resin systems, but fractural behaviour was complicated depending on both PMS MW and concentration. The use of PMS (10 wt%) with low or medium MW led to *ca* 30% increase in K_{IC} with no sacrifice of mechanical and thermal properties of the modified resins and the modified resins had two-phase morphologies. In the modification with PMS of low or medium MW, the extent of the improvement in the toughness is comparable to the fractural behaviour in the modification with the reactive acrylic elastomers, BA–GMA–AN terpolymers, previously reported as effective modifiers [8]. In the modification with higher MW PMS, the fractural behaviour changed drastically depending on PMS concentration (Fig. 1). On addition of 5 wt% of PMS with $\bar{M}_w > 231{,}000$, the extent of toughening is comparable or slightly larger than when using lower MW PMS. In the use of 10 wt% of higher MW PMS, K_{IC} increased significantly. PMS of $\bar{M}_w$ 345,000 is the most effective modifier and its 10 wt% inclusion led to 130% increase in K_{IC}, whereas K_{IC} increased by 50% on 5 wt% addition. The dependence of K_{IC} on PMS concentration in the higher-MW PMS modification systems is quite different from that in the modification of epoxies with reactive acrylic elastomers, where K_{IC} increased gradually with increasing elastomer concentration [4–8]. In the modification with PMS of $\bar{M}_w > 231{,}000$, K_{IC} increased rather discontinuously with increase in PMS concentration (Fig. 2).

The morphological behaviour of the modified resins is interesting and it is instructive to consider the toughening mechanism in the present systems. The morphologies of the modified resins changed drastically, dependent on both PMS MW and concentration. On addition of 5 wt% of PMS, the modified resins had two-phase morphologies with PMS-rich spherical particles dispersed in the epoxy matrix, independent of MW of PMS used. Inclusion of 10 wt% of PMS led to drastic change in the morphology of the modified resins, dependent on PMS MW; when using PMS with $M_w < 150{,}000$, two-phase

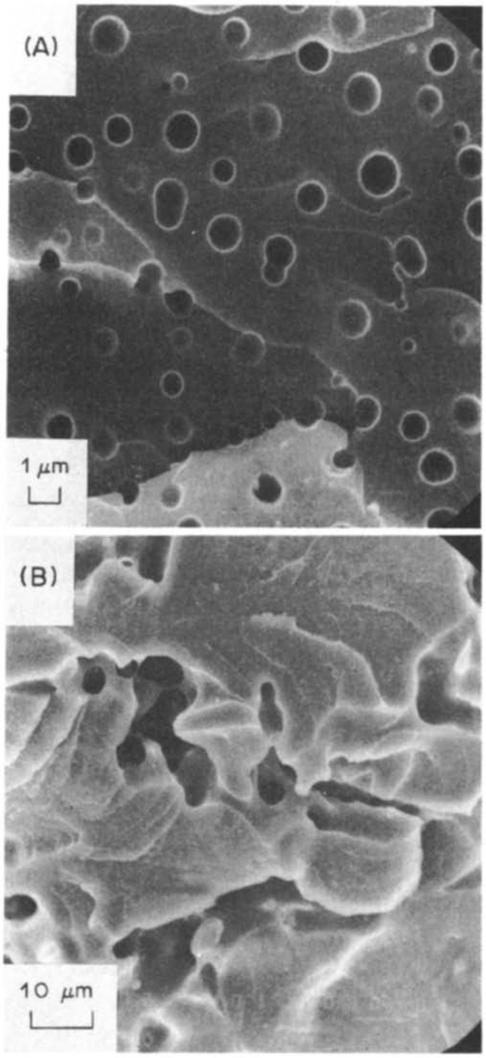

Fig. 6. SEMs of fracture surfaces for the cured resins modified with PMS, etched with THF. Amount of PMS ($\bar{M}_w$ 344,000): A, 7 wt% addition; B, 10 wt% addition.

morphologies were observed but PMS particles tended to coagulate and form the co-continuous phase in the modification with higher MW PMS (Fig. 4). These morphological behaviours correspond to the dependence of K_{IC} on PMS MW (Fig. 1). The effect of PMS concentration on the morphological behaviour was investigated in detail for the most effective modifier ($\bar{M}_w$ 344,000) (Fig. 5). In the use of higher MW PMS, two phase morphologies were observed on addition of <7 wt% of the modifier. On addition of 8 wt% of PMS, the PMS-rich particles began to coagulate, though a small amount of the particles still remained in the epoxy matrix. In the use of 10 wt% of PMS, a larger amount of the particles formed the co-continuous phase, together with significant increase in K_{IC} (Fig. 3). The PMS-rich particles and continuous phase in the modified resins were removed by etching (Fig. 6). This fact indicates that there is no chemical interfacial adhesion between the epoxy matrix and PMS. In the present modification system, flexural modulus and T_g did not decrease on modification but the use of effective PMS with higher MW led to a medium decrease in flexural strength, which could be explained by insufficient adhesion between the matrix and the modifier, based on physical interactions such as van der Waals forces. It is thought that such deficiency would be overcome by introducing functional groups into the modifier.

Dynamic viscoelastic analysis indicates the presence of phase-separation. It is thought that the shoulder peak at *ca* 175–185° in the tan δ curve must be due to PMS-rich phase, but its transition temperature is lower than T_g (DSC) of PMS. Such dynamic viscoelastic behaviour was observed in the modification of epoxies with poly(etherimide)s where it was explained on the basis of plasticization by a low molecular weight species such as unreacted epoxies [3, 15]. In this study, the volume fraction of PMS-rich particles is larger than the weight fraction of PMS (Fig. 4). This also indicates incorporation of epoxies into the particles.

Fractural behaviour corresponds to the morphology of the modified resins. In every case in this study, the toughness of epoxy resin could be improved to a considerable extent because of the co-continuous structure of the modified resins. These results suggest that two toughening mechanisms could operate in the present modification system; one mechanism is based on two phase separation structure and similar to that in the rubber-modification systems [1] and the other mechanism is based on the co-continuous phase morphology. The latter mechanism would be similar to that in the modification of epoxies with engineering thermoplastics such as poly(etherimide)s [3, 15] and poly(ether ketone)s [18]. In the modification of tetraglycigyl-4,4′-diaminodiphenyl methane with poly(etherimide)s (Ultem 1000, GE) (PEI), K_{IC} for the cured resin modified with 25 phr of PEI increased 180%, where the phase inversion of morphologies was observed and the toughening of epoxies could be achieved by the absorption of fractural energy due to ductile drawing and tearing of the thermoplastic 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 co-continuous structure due to the spinodal decomposition was formed in the modified resin with PPDE of higher MW ($\bar{M}_{GPC}$ 56,300), together with a significant increase in K_{IC} [18].

Engineering thermoplastics have high T_g because of their rigid structures. PMS also has 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 epoxy resin; in general, the use of a small amount of solvent is essential to dissolve the thermoplastics into epoxies in the modification with the thermoplastics. All samples of PMS used in this study were soluble in the epoxy resin without using solvents and PMS of $\bar{M}_w > 231{,}000$ is comparable as a modifier to the engineering thermoplastics such as poly(etherimide)s. The effectiveness of PMS as a modifier could be explained by its similar structure to PEI, where the polar imide units in PEI and PMS would play an

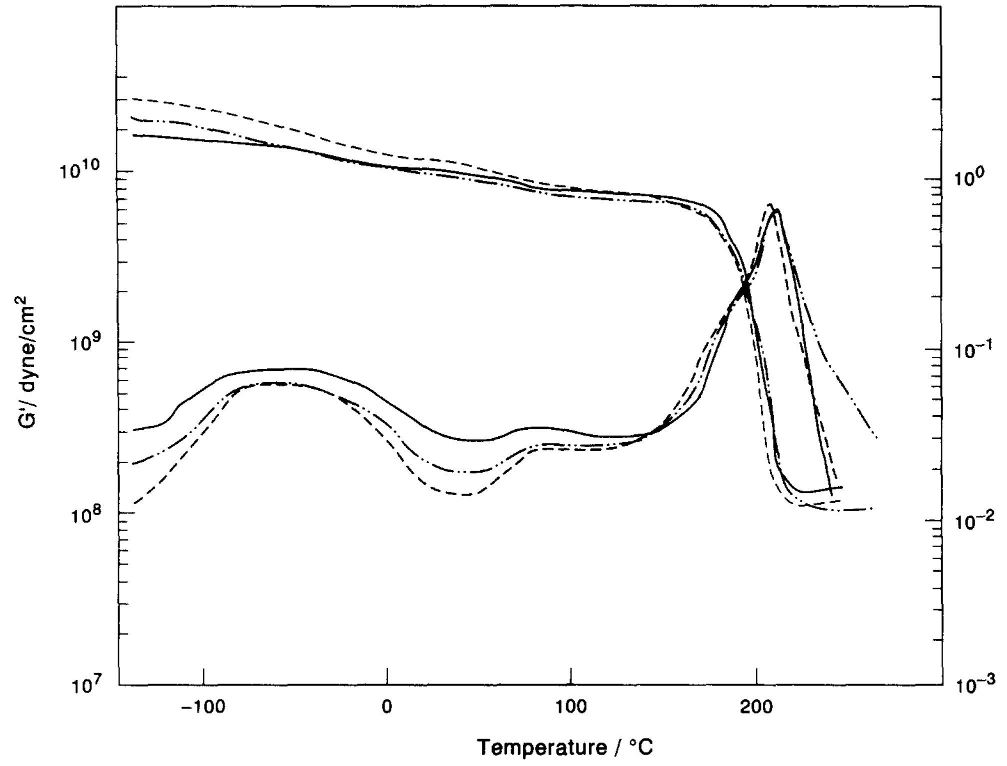

Fig. 7. Dynamic viscoelastic analysis for unmodified and PMS-modified resins. PMS, $\bar{M}_w$ 344,000; (——) control, (- - -) 5 wt% addition, (—··—) 10 wt% addition.

important role in the physical interfacial adhesion between the epoxy matrix and the thermoplastics.

The T_g values for the resins modified with PMS are equal to or higher than that for the unmodified epoxy resin.

In conclusion, PMS is an interesting and effective modifier for improving the toughness of epoxy resins. Two toughening mechanisms operate in the present system dependent 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 DGEBA resin can be attained by the latter phase structure. The most suitable composition for modification of the epoxy resin was inclusion of 10 wt% of PMS with $\bar{M}_w$ 344,000. The drawback in the present modification system is the medium decrease in the flexural strength, perhaps caused by rather poor interfacial adhesion between the epoxy matrix and PMS. It is thought that the efficiency of the modifier would be increased by enhancing interfacial adhesion by chemical bonding.

Acknowledgements—The authors thank Dr Shinji Takeda (Hitachi Chemical Industrial Co., Ltd) for dynamic viscoelastic analyses and Dr Misao Hiza (Yokohama Rubber Co., Ltd) for the recording of SEMs.

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