Eur. Polym. J. Vol. 29, No. 8, pp. 1103–1113, 1993
Printed in Great Britain. All rights reserved

0014-3057/93 \$6.00 + 0.00

EFFECT OF CROSS-LINK DENSITY ON MODIFICATION OF EPOXY RESINS BY *N*-PHENYLMALEIMIDE–STYRENE COPOLYMERS

TAKAO IIJIMA,* SATORU MIURA, WAKICHI FUKUDA and MASAO TOMOI
Department of Applied Chemistry, Faculty of Engineering, Yokohama National University, Tokiwadai 156, Hodogaya-ku, Yokohama 240, Japan

(Received 22 September 1992)

Abstract—The effect of cross-link density on the toughening of modified resins was investigated for the modification of epoxy resins with *N*-phenylmaleimide–styrene alternating copolymers (PMS). The cross-link density of the epoxy matrix was controlled by a combination of two kinds of epoxy resins [diglycidyl ether of bisphenol-A (DGEBA) or triglycidyl aminocresol (TGAC)] and hybrid hardeners composed of *p,p'*-diaminodiphenyl sulphone (DDS) and *p,p'*-(*N,N'*-dimethyl)-diaminodiphenyl sulphone (MDS). The addition of 10 wt% of PMS ($\bar{M}_w$ 214,000) led to 120% increase in the fracture toughness (K_{IC}) of the DGEBA resin cured with the hybrid hardener (DDS:MDS, 67:33 mol ratio). On addition of 15 wt% of PMS ($\bar{M}_w$ 214,000), K_{IC} for the modified resin increased 110% in the TGAC/hybrid hardener (DDS:MDS, 67:33 mol ratio) system. Morphologies of the modified resins depended on PMS molecular weight and concentration, and the cross-link density of the matrix. The toughening of epoxies could be explained by the cocontinuous phase structure in every case.

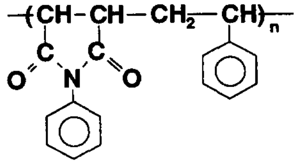
INTRODUCTION

Epoxy resins are some of the most important thermosetting polymers and have wide use as structural adhesives and matrix resins for fibre composites but the cured resins have one drawback; they are brittle and have poor resistance to crack propagation. The toughness of bifunctional epoxy resins such as diglycidyl ether of bisphenol-A (DGEBA) has been increased by blending with reactive liquid rubbers such as carboxyl-terminated butadiene-acrylonitrile rubbers (CTBN) [1] but CTBN have been reported as less effective modifiers in the toughening of a highly cross-linked epoxy matrix [2].

In previous papers, various kinds of epoxy-containing acrylic elastomers have been reported as improving the toughness of *p,p'*-diaminodiphenyl sulphone (DDS)-cured epoxy resins, where vinylbenzyl glycidyl ether and glycidyl (meth)acrylate were used as epoxy-containing monomers [3–7]. It is noteworthy that these reactive elastomers were effective even in the modification of DDS-cured DGEBA epoxy resins with moderate cross-link structure having glass transition temperature over 180°, whereas CTBN is effective only in a rather lightly cross-linked matrix such as piperidine-cured DGEBA resins, and less effective in the modification of DGEBA/DDS systems [2]. The epoxy-containing reactive elastomers were less effective in the highly cross-linked epoxy matrix formed from triglycigyl aminocresol (TGAC)/DDS mixtures [7].

Engineering thermoplastics are interesting materials as modifiers in epoxy resins for the maintenance of mechanical and thermal properties for the matrix resins. Various types of ductile thermoplastics have been used as alternatives to reactive rubber for improving the toughness of epoxy resins; they include poly(ether sulphone)s [8–12], poly(etherimide) [13–16], poly(aryl ether ketone)s [17, 18], poly(phenylene oxide) [19] and aromatic polyesters [20]. Recently, we have found that *N*-phenylmaleimide–styrene copolymers (PMS) [21] and *N*-phenylmaleimide-*N*-cyclohexylmaleimide–styrene terpolymers (PCMS) were effective modifiers for DGEBA epoxy resins [22]. In the modification with both PMS and PCMS, morphologies of the modified resins changed, giving two-phase or cocontinuous phase structure according to the molecular weight and concentration of the modifiers. The improvement in the toughness of the modified resins was larger in the latter structure than in the former. In spite of the C—C bond repeating units, PMS and PCMS have T_gs over 200° because of the steric restriction to molecular motion of the main chain caused by the bulky side groups. Furthermore, the high molecular weight polymers could be easily prepared by radical copolymerization, whereas it is rather difficult to obtain engineering thermoplastics with high molecular weights, as they are generally prepared by polycondensation.

This paper reports the effect of the cross-link density on the modification with PMS of DDS-cured epoxy resins. The cross-link density of the epoxy matrix could be controlled using two kinds of epoxy resins (DGEBA or TGAC) or the hybrid hardeners [DDS and *p,p'*-(*N,N'*-dimethyl)diaminodiphenyl sulphone (MDS)].



PMS

---

*To whom all correspondence should be addressed.

Table 1. Preparation and characterization of PMS*

Entry No.	$C_{12}H_{25}SH$† (mol%)	Yield (%)	$\bar{M}_w$‡ (10^4)	$\bar{M}_n$‡ (10^4)	$\bar{M}_w/\bar{M}_n$	T_g§ (°C)
1¶	1.0	98	3.6	1.4	2.67	211
2	0.78	91	5.7	2.6	2.27	215
3	0.4	87	10.9	4.5	2.41	220
4	0.2	90	15.0	6.4	2.35	222
5¶	0.2	96	21.4	5.6	3.85	216
6	0.1	90	23.0	10.6	2.17	223
7	0.03	92	28.9	13.0	2.21	221

*Feed composition, PMI:St 1:1 mol ratio; in acetone at 60°.
†Chain transfer agent.
‡By GPC.
§By DSC.
¶In benzene at 70°.

EXPERIMENTAL PROCEDURES

Materials

The epoxy resins were the liquid bisphenol-A diglycidyl ether (DGEBA) [Epikote 828, Shell Chemical Industrial Co., epoxy equivalent weight (EEW) 190] and triglycidyl aminocresol (TGAC) (ELM-100, Sumitomo Chemical Industrial Co., EEW 113). DDS and MDS were used as curing agents; MDS was prepared by the reaction of 4,4′-dichlorodiphenyl sulphone and monomethylamine [7]. *N*-Phenylmaleimide (PMI) was provided by Nippon Shokubai Corporation. Styrene (St) was purified in the usual way. PMS was prepared from a 1:1 mol feed of PMI and St as reported previously [21]. Other reagents were used as received.

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. 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 (T_g) of both copolymers and cured resins were measured by differential scanning calorimetry (Shimadzu DSC 41 M type) at a heating speed of 10°/min except for cured TGAC resins. T_g for the TGAC resins was obtained by thermal mechanical analysis (Shimadzu TMA 40 M type) at a heating speed of 5°/min. Scanning electron micrographs were taken with 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 250° at a heating speed of 5°/min at a frequency of 1 Hz.

Curing procedure

PMS was dissolved in the epoxy resin without solvents by heating at 140°. Then the curing agents, DDS and MDS, were added to the mixture, which was kept at 120° for about 1 hr to dissolve DDS. The resulting clean mixture was poured into a silicon mould preheated at 100°. The curing cycle was 120°/1 hr followed by 180°/5 hr. The amount (wt%) of PMS used was based on the epoxy resin. The curing agents were used stoichiometrically to the epoxy resin.

RESULTS

Mechanical and thermal properties of modified epoxy resins

It has been reported that the copolymerization of PMI and styrene give alternating copolymers, independent of the feed monomer composition [21, 23]. Table 1 reports some characteristic properties of the copolymers. T_g of PMS was in the range of 211–223°.

Table 2 shows representative results for the modification of the DGEBA resin with PMS. The cured DGEBA resin was transparent but the modified resins became translucent. In the modification with PMS of low molecular weight (MW) ($\bar{M}_w$, 36,000), K_{IC} for the DDS-cured resin increased 30% at no expense of mechanical and thermal properties of the modified resin on 10% addition. When using the hybrid hardener, K_{IC} increased 50% with a decrease in T_g (Entry No. 4). The use of 10 wt% of high $\bar{M}_w$ PMS (214,000) led to a significant increase (100%) in K_{IC} for the DDS-cured resin with a medium decrease in flexural strength, compared with the unmodified DGEBA resin. When using the hybrid hardener, K_{IC} for the modified resin increased 120% with a slight decrease in T_g (Entries Nos 5 and 6).

Figures 1 and 2 show the mechanical and thermal properties of the cured DGEBA resin as a function of PMS concentration; the results for the DDS-cured resins modified with low molecular weight PMS ($\bar{M}_w$ 36,000) have been reported previously [21]. In the modification system with low MW PMS, K_{IC} for the modified resins increased gradually with PMS concentration. When using the hybrid hardener (DDS:MDS, 65:35 NH ratio), K_{IC} for the modified resins increased slightly. In the modification with 10 wt% of high MW PMS ($\bar{M}_w$ 214,000), K_{IC} for the DDS-cured resin increased 105%, compared to that

Table 2. Mechanical and thermal properties of cured DGEBA resins*

Entry No.	1	2	3	4	5	6
Composition (wt ratio)						
DGEBA/PMS	100/0	90/10	100/0	90/10	90/10	90/10
(PMS MW)	(—)	(36,000)	(—)	(36,000)	(214,000)	(214,000)
Hardener composition						
DDS/MDS (mol ratio)	100/0	100/0	48/52	48/52	100/0	67/33
(NH ratio)	100/0	100/0	65/35	65/35	100/0	75/25
Flexural strength (kgf/mm^2)	15.3 ± 1.0	14.7 ± 1.1	15.5 ± 0.3	15.3 ± 0.3	10.2 ± 0.5	10.4 ± 0.3
Flexural modulus (kgf/mm^2)	304 ± 13	300 ± 8	293 ± 10	303 ± 7	311 ± 10	312 ± 9
n†	6	6	9	7	7	6
K_{IC} (MN m$^{-3/2}$)	0.70 ± 0.05	0.93 ± 0.04	0.71 ± 0.04	1.07 ± 0.06	1.43 ± 0.06	1.57 ± 0.06
n†	9	6	6	5	7	8
T_g‡ (°C)	180 (200§)	183	144	143	181	161

*The ±x values show standard deviations.
†Number of specimens.
‡By DSC.
§By TMA. Ref. [7].

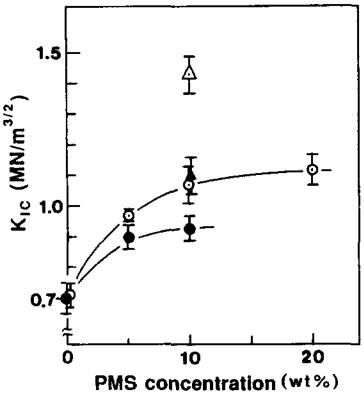


Fig. 1. Fracture toughness for modified resins as function of PMS concentration in the DGEBA modification. ●, PMS ($\bar{M}_w$ 36,000), DDS only; ⊙, PMS ($\bar{M}_w$ 36,000), DDS/MDS 65:35 NH ratio; △, PMS ($\bar{M}_w$ 214,000), DDS only; ▲, PMS ($\bar{M}_w$ 214,000), DDS/MDS 65:35 NH ratio.

for the unmodified DDS-cured resin but the use of the hybrid hardener led to a decrease in K_{IC} for the modified resin (Fig. 1). When using 15 wt% of high MW PMS (214,000), the cured resin could not be obtained because of the increased viscosity of the uncured epoxy mixture at 120°. The flexural strength for the low MW PMS-modified resins hardly changed up to 10 wt% addition of PMS, independent of hardener composition, and then decreased slightly on 20 wt% addition, compared to that for the unmodified DDS-cured DGEBA resin. Flexural moduli for the modified resins hardly changed (Fig. 2). In the modification with high MW PMS, the flexural strength decreased but the flexural modulus was maintained. T_gs for the DDS-cured resins did not decrease as a result of the PMS modification. T_gs for the hybrid hardener-cured resins decreased compared to those for the DDS-cured resins.

Figures 3 and 4 show the dependence of the mechanical and thermal properties of the high MW PMS-modified resins on the hardener composition in the DGEBA modification system. K_{IC} for the unmodified resins hardly changed with the hybrid hardener composition as reported previously [7]. K_{IC} for thePMS (10 wt%)-modified resin increased 100% in the DGEBA/DDS system. On addition of 10 wt% of PMS ($\bar{M}_w$ 214,000], K_{IC} for the modified resins increased gradually with increasing MDS content up to 33 mol% in the hybrid hardener system (120% increase in the DDS/MDS 67:33 mol ratio, 75:25 NH ratio) compared to that for DDS-cured unmodified DGEBA resin; the use of greater MDS content led to a considerable decrease in K_{IC} (Fig. 3). The flexural strength for the modified resin decreased but the flexural modulus hardly changed compared to that for the unmodified DGEBA resin (Fig. 4). T_gs for the cured resins decreased with increasing MDS content.

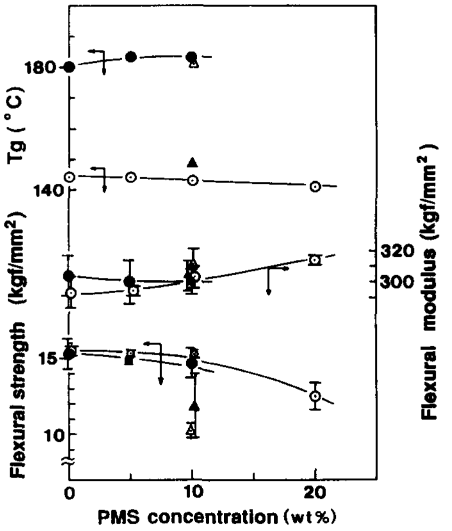


Fig. 2. Physical properties for modified resins as function of PMS concentration in the DGEBA modification. ●, PMS ($\bar{M}_w$ 36,000), DDS only; ⊙, PMS ($\bar{M}_w$ 36,000), DDS/MDS 65:35 NH ratio; △, PMS ($\bar{M}_w$ 214,000), DDS only; ▲, PMS ($\bar{M}_w$ 214,000), DDS/MDS 65:35 NH ratio.

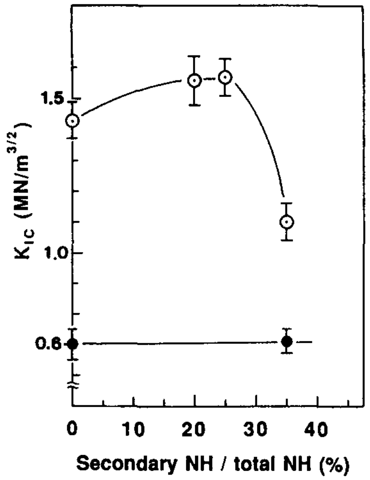


Fig. 3. Dependence of fracture toughness for modified resins on the hardener composition in the DGEBA modification. ●, Unmodified resin; ⊙, PMS ($\bar{M}_w$ 214,000) 10 wt% addition.

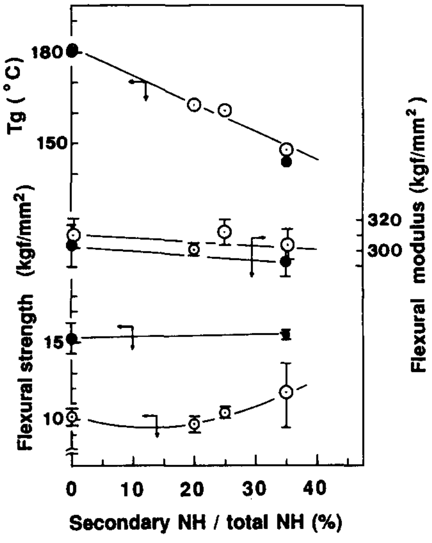


Fig. 4. Dependence of physical properties for modified resins on the hardener composition in the DGEBA modification. ●, Unmodified resin; ⊙, PMS ($\bar{M}_w$ 214,000) 10 wt% addition.

Table 3. Mechanical and thermal properties of cured TGAC resins*

Entry No.	1†	2	3	4	5	6
Composition (wt ratio)						
TGAC/PMS	100/0	100/0	90/10	85/15	90/10	85/15
(PMS MW)	(—)	(—)	(214,000)	(214,000)	(214,000)	(214,000)
Hardener composition						
DDS/MDS (mol ratio)	100/0	48/52	100/0	100/0	48/52	48/52
Flexural strength (kgf/mm^2)	16.4 ± 0.4	16.7 ± 1.9	7.6 ± 0.4	6.0 ± 0.2	15.3 ± 1.2	6.6 ± 0.3
Flexural modulus (kgf/mm^2)	431 ± 13	411 ± 7	440 ± 12	440 ± 10	412 ± 9	435 ± 8
n‡	6	7	7	6	5	7
K_{IC} (MN m$^{-3/2}$)	0.61 ± 0.04	0.61 ± 0.02	1.04 ± 0.02	1.22 ± 0.05	0.80 ± 0.06	1.26 ± 0.05
n‡	5	7	5	7	5	8
T_g§ (°C)	237	199	207	177	175	169

*The ±*x* values show standard deviations.
†Ref. [7].
‡Number of specimens.
§By TMA.

Table 3 shows representative results for the modification of the TGAC resins with PMS. The unmodified cured TGAC resins were transparent and the modified resins were translucent. K_{IC} for the modified resin increased 100% with a significant decrease in flexural strength, when using 15 wt% of higher MW PMS ($\bar{M}_w$ 214,000) (Entry No. 4). K_{IC} for the PMS (15 wt%)-modified resin in the TGAC/hybrid hardener system was similar to that in the TGAC/DDS modification (Entries Nos 4 and 6). Flexural moduli for the modified resins hardly changed relative to that for unmodified DDS-cured TGAC resin. T_gs for unmodified and modified resin decreased with increasing MDS content.

Figure 5 shows the dependence of K_{IC} on the PMS (10 wt%) MW in the TGAC/DDS system. The improvement in toughness of the cured TGAC resin was slight (*ca* 10% increase) when using PMS with $\bar{M}_w < 150{,}000$. K_{IC} for the modified resin increased significantly on addition of higher MW PMS: inclusion of 10 wt% of PMS ($\bar{M}_w$ 214,000) led to a 70% increase in K_{IC}. The flexural strength for the modified resin increased slightly when using low MW PMS but decreased on modification with high MW PMS (Fig. 6). Flexural moduli for the modified resins were comparable to that for the unmodified DDS-cured TGAC resin. T_gs for the modified resins decreased slightly in every case, compared to that for the unmodified DDS-cured TGAC resin.

Figures 7 and 8 show the dependence of the mechanical and thermal properties of the high MW PMS-modified resins on the hardener composition in the TGAC modification system. K_{IC} for the unmodified resin hardly changed with the hardener composition. When using 10 wt% of higher MW PMS (214,000), K_{IC} for the modified resin decreased significantly on addition of a small amount of MDS (10 NH%) and then increased slightly with increasing MDS content (Fig. 7). On addition of 15 wt% of PMS (MW 214,000), K_{IC} increased gradually with increasing MDS content. The flexural strength for the PMS (10 wt%)-modified resin increased together with decrease in K_{IC}. Flexural moduli for the modified resins were comparable to or less than that for the unmodified DDS-cured TGAC resin (Fig. 8). T_gs for the modified resins decreased with increasing MDS content.

Figures 9 and 10 show the mechanical and thermal properties of the cured TGAC resins as a function of the PMS (214,000) concentration. The cured resins could not be prepared because of the high viscosity of the uncured epoxy mixture at 120°, when using 20 wt% of PMS. K_{IC} for the modified resins increased discontinuously with increasing PMS concentration. The decrease in flexural strength for the modified resins was inversely proportional to the increase in

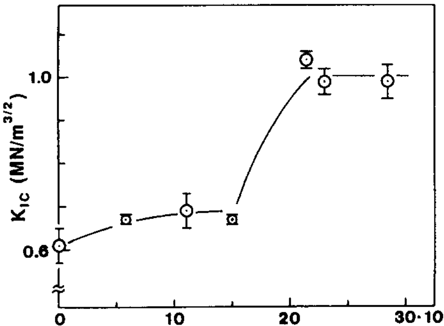


Fig. 5. Dependence of fracture toughness for modified resins on the PMS molecular weight in the TGAC modification. PMS 10 wt% addition, DDS only.

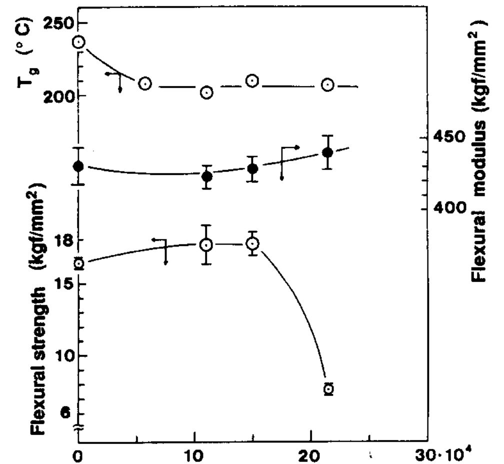


Fig. 6. Dependence of physical properties for modified resins on the PMS molecular weight in the TGAC modification. PMS 10 wt% addition, DDS only.

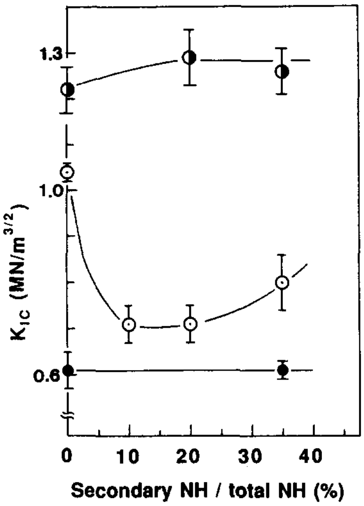


Fig. 7. Dependence of fracture toughness for modified resins on the hardener composition in the TGAC modification. ●, Unmodified resin; ○, PMS ($\bar{M}_w$ 214,000) 10 wt% addition; ◑, PMS ($\bar{M}_w$ 214,000) 15 wt% addition.

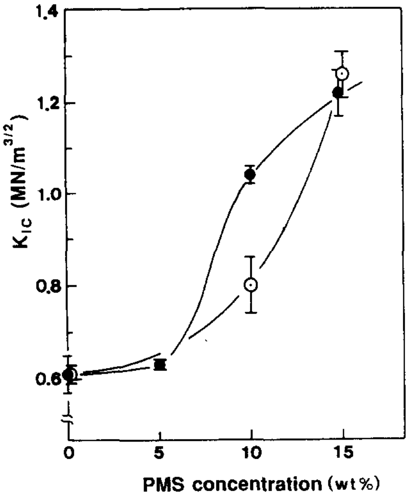


Fig. 9. Fracture toughness for modified resins as function of PMS concentration in the TGAC modification. PMS ($\bar{M}_w$ 214,000); ●, DDS only; ○, DDS/MDS 65:35 NH ratio.

K_{IC}. The flexural modulus for the DDS-cured modified resin was comparable to that for the unmodified TGAC resin. With the hybrid hardener system, the flexural modulus increased slightly on addition of 15 wt% of PMS. T_g for the cured resin decreased when using the hybrid hardener. T_g for the modified resin decreased gradually with increasing PMS concentration.

Morphologies of modified epoxy resins

The morphologies of the cured resins were investigated by scanning electron microscopy (SEMs). The parent epoxy resins had only one phase as reported previously [3]. Inclusion of PMS led to phase separation in the cured resins. The morphologies of the cured resins changed drastically, depending on the hardener composition and the PMS MW and concentration.

Figure 11 shows SEMs of the cured DGEBA resins modified with 10 wt% of PMS (214,000) in the hybrid hardener system. The PMS-modified resin had a cocontinuous phase morphology up to addition of 33 mol% of MDS (25 NH%) [Fig. 11(A)–(C)] and the PMS-rich phase consisted of an aggregation of small PMS particles. When using 52 mol% of MDS (35 NH%), the modified resin had a two-phase

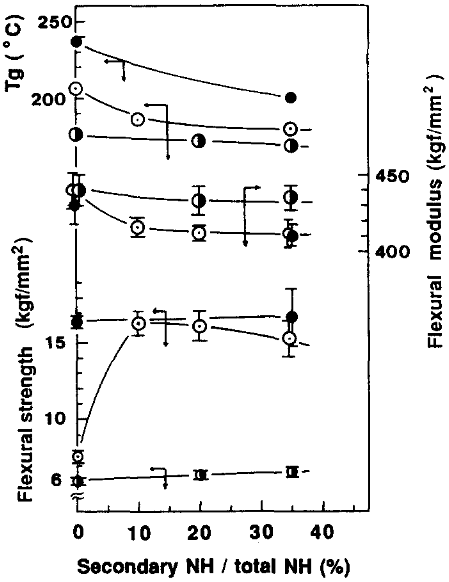


Fig. 8. Dependence of physical properties for modified resins on the hardener composition in the TGAC modification. ●, Unmodified resin; ○, PMS ($\bar{M}_w$ 214,000) 10 wt% addition; ◑, PMS ($\bar{M}_w$ 214,000) 15 wt% addition.

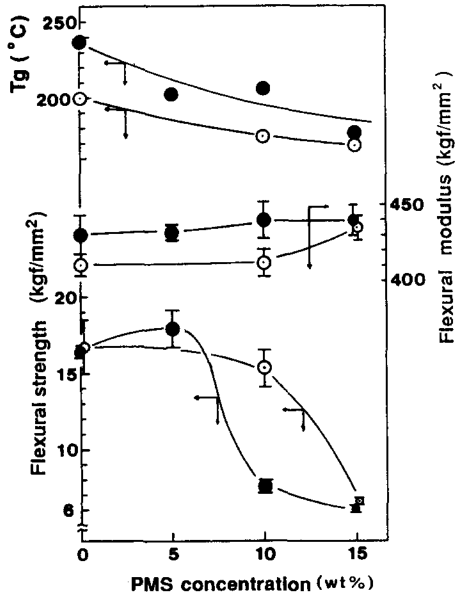


Fig. 10. Physical properties for modified resins as function of PMS concentration in the TGAC modification. PMS ($\bar{M}_w$ 214,000); ●, DDS only; ○, DDS/MDS 65:35 NH ratio.

structure with PMS-rich spherical particles dispersed in the epoxy-rich matrix; the volume fraction (V_f) and the average diameter (D) of the particles were 0.20 and 1.17 μm for 10 wt% addition of PMS [Fig. 11(D)].

In the TGAC/DDS modification system, the lower MW (150,000) PMS (10 wt%)-modified resin had two-phase morphology; V_f and D were 0.14 and 1.32 μm [Fig. 12(A)]. The use of higher MW PMS (214,000) led to a drastic change in the morphology of the modified DDS-cured resin; the modified resin was two-phase on 5 wt% addition of PMS (V_f and D are 0.09 and 1.10 μm) [Fig. 12(B)] and the cocontinuous morphology was observed for >10 wt% addition of PMS [Fig. 12(C) and (D)]. On addition of 10 wt% of high MW PMS (214,000), the modified resin had two-phase morphology in the hybrid hardener system; V_f and D were 0.14 and 1.23 μm for the DDS/MDS (90:10 NH ratio) hardener system, and 0.17 and 1.32 μm for the DDS/MDS (65:35 NH ratio) system [Fig. 13(A) and (B)]. When using 15 wt% of PMS (MW 214,000), the modified resin had the cocontinuous phase structure even with the hybrid hardener system (DDS/MDS, 65:35 NH ratio) [Fig. 13(C)].

Dynamic viscoelastic analysis of modified epoxy resins

Dynamic viscoelastic analysis can give information on the micro-structure of cured resins. Figure 14 shows the storage moduli, G', and tan δ for the unmodified and PMS (214,000)-modified DGEBA resins. The peak position of the α-relaxation in the tan δ curves shifted towards lower temperature in the hybrid hardener system and a shoulder peak was observed above 200°. The equilibrium storage modulus in the rubber region above T_g was not clear because of the presence of the shoulder peak. The cross-link density of the modified resins could not be obtained in the DGEBA/PMS system. The storage moduli in the glass state were comparable to that for

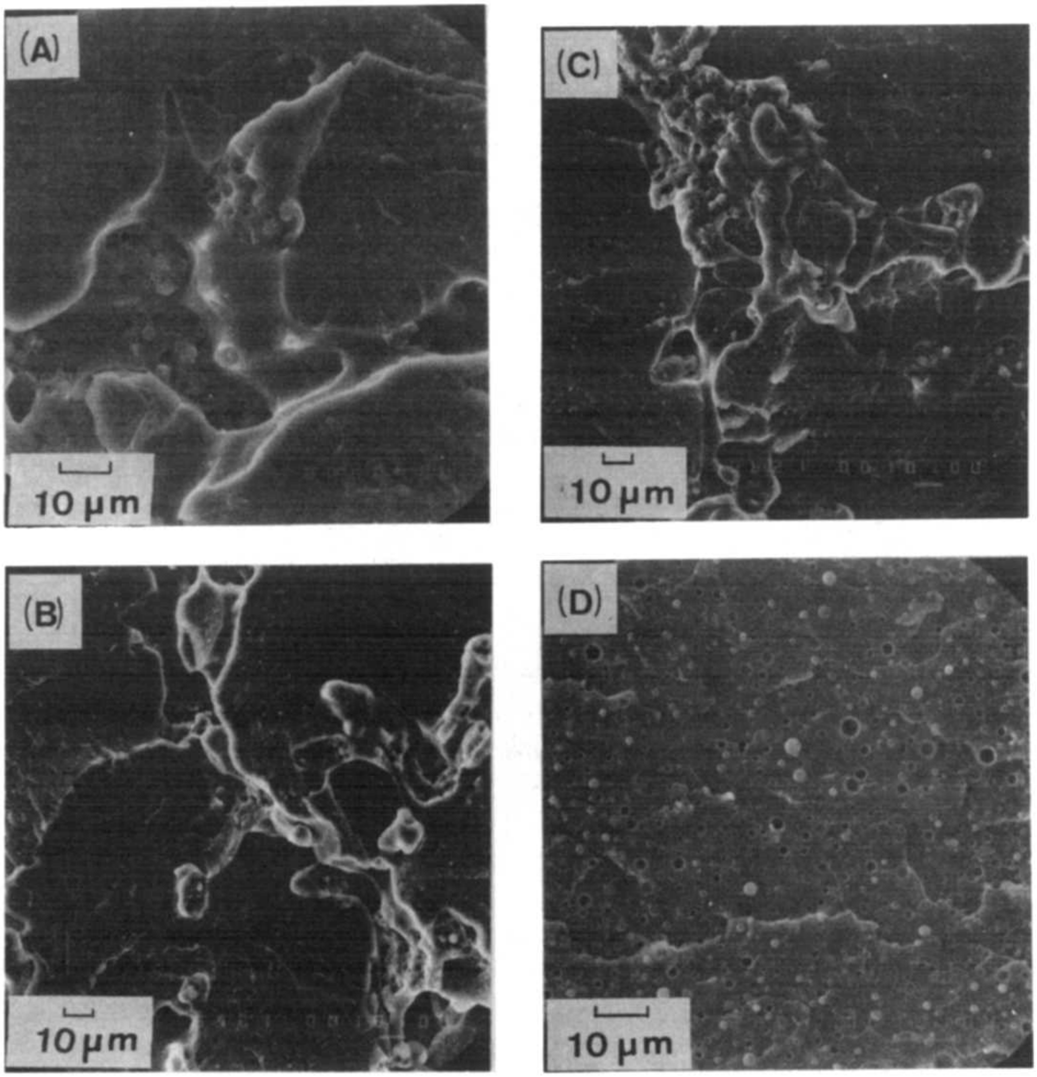


Fig. 11. SEMs of fracture surfaces for the cured DGEBA resins modified with 10 wt% of PMS. PMS $\bar{M}_w$ 214,000; (A) DDS only; (B) DDS/MDS 80:20 NH ratio; (C) DDS/MDS 75:25 NH ratio; (D) DDS/MDS 65:35 NH ratio.

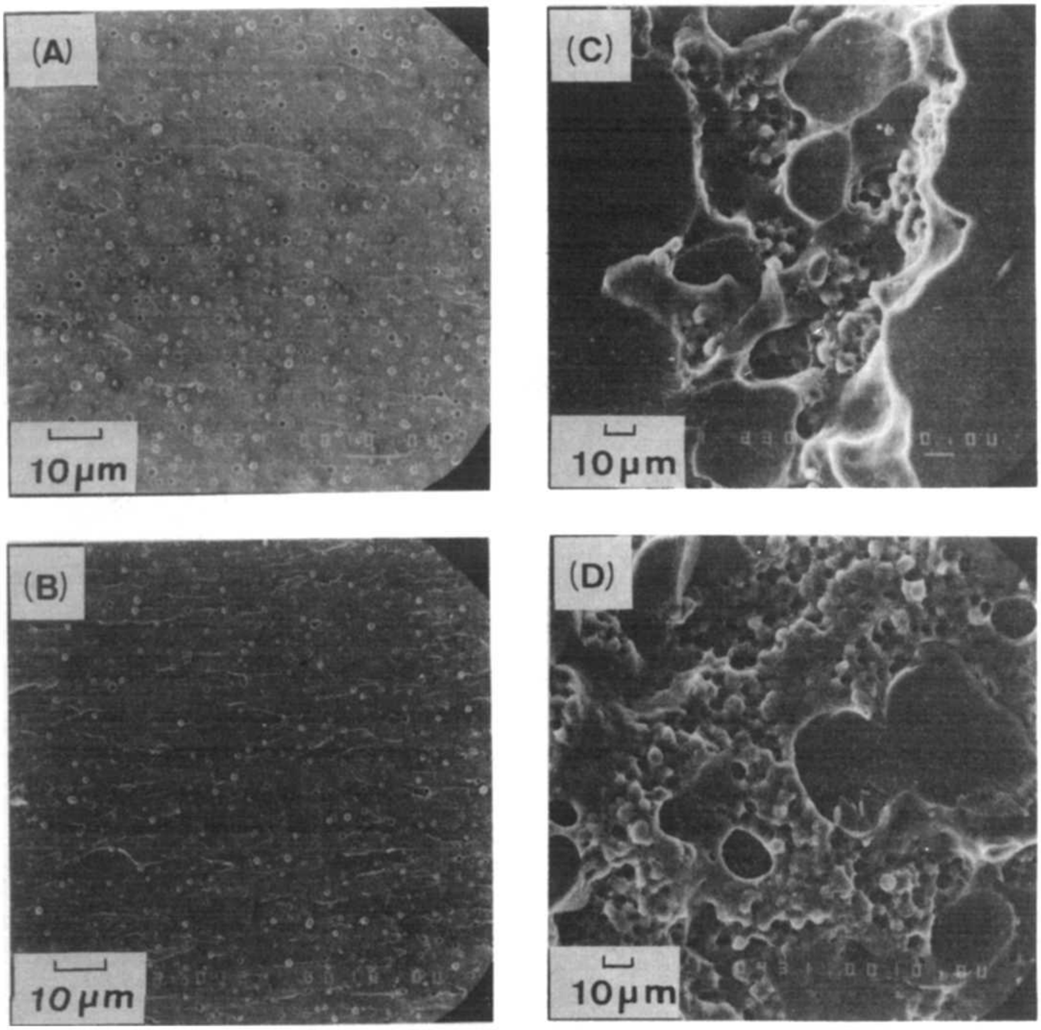


Fig. 12. SEMs of fracture surfaces for the DDS-cured TGAC resins modified with PMS. (A) PMS ($\bar{M}_w$ 150,000), 10 wt% addition; (B) PMS ($\bar{M}_w$ 214,000), 5 wt% addition; (C) PMS ($\bar{M}_w$ 214,000), 10 wt% addition; (D) PMS ($\bar{M}_w$ 214,000), 15 wt% addition.

the unmodified resin. In the modification of TGAC with PMS, the α-relaxation temperature in the tan δ curves hardly changed and the α'-relaxation appeared at 211° (Fig. 15). The equilibrium storage modulus in the rubber region could not be obtained perhaps because of heat instability of the TGAC matrix. The α-relaxation peak position in the tan δ curves shifted toward lower temperature when using the hybrid hardener and a shoulder was observed at *ca* 187°. The equilibrium storage modulus for the modified resin was smaller than that for the unmodified resin in the TGAC/hybrid hardener system.

DISCUSSION

PMS is a new effective modifier for improving the toughness of the DDS-cured DGEBA resin with moderate cross-link density as reported previously [21]. The morphology of the DDS-cured resin modified with PMS changed drastically, depending on both PMS MW and concentration. The fractural behaviour depends on the morphology of the modified resin. Two toughening mechanisms operate in the DGEBA/DDS modification system; one mechanism is based on a two phase separation structure, similar to that in the rubber-modification systems [1]; the other mechanism is based on the cocontinuous phase morphology. The most effective modification can be reached by the latter phase structure.

It is important to study the dependence of the effectiveness of the modifier on the cross-link density of the matrix when considering use as structural adhesives, because reactive elastomers are less effective in the highly cross-linked epoxy matrix [1, 2, 7]. Dynamic viscoelastic analyses were carried out to examine the cross-link density of the matrix in the PMS modification systems (Figs 14 and 15). 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.* In the DGEBA/hybrid hardener/PMS system, the cross-link density could not be obtained because of the presence of the shoulder peak at *ca* 215° based on PMS (Fig. 14). In the TGAC/DDS system, the equilibrium storage moduli in the rubber region could not be observed over the α-relaxation temperature (266°) in the tan δ curves for the cured resins perhaps because of heat instability of the TGAC matrix and the cross-link density could not be obtained (Fig. 15). When using the hybrid hardener (DDS/MDS), 65:35 NH ratio), the cross-link density (mol/cm^3) of the unmodified TGAC resin was 2.81×10^{-3} and higher than that (1.58×10^{-3}) of the unmodified DGEBA resin. When using the hybrid hardener of the same composition, the cross-link density (2.08×10^{-3}) of the modified TGAC resin decreased on addition of 10 wt% of PMS (214,000) compared to that of the unmodified TGAC resin. In the DDS/MDS hybrid hardener system, the cross-link density of the cured DGEBA resins can be controlled systematically by using MDS as reported previously [7]. Figure 16 shows the relationship between the hybrid hardener composition and the cross-link density for the unmodified DGEBA resins [7], where the cross-link density for the cured resins decreases linearly with increasing MDS content as does T_g also; T_g is a measure of the cross-link density of the cured resin. Though the cross-link density could not be obtained for both the DGEBA/hybrid hardener/PMS system and the DDS-cured TGAC resins, the T_g values for the cured resins indicate the change in cross-link density. A plot of T_g for the cured resin against the hybrid hardener composition is linear for the DGEBA/PMS modification (Fig. 16). This linear relation shows that the cross-link density would also decrease linearly with increasing MDS content in the DGEBA/hybrid hardener/PMS system. The peak position in the tan δ curve is 203° for the unmodified DDS-cured DGEBA resin and 266° for the unmodified DDS-cured TGAC material. The cross-link density of the latter matrix is higher than that of the former resin. In the TGAC/hybrid hardener/PMS system, T_gs for the modified resins decreased with increasing MDS content (Fig. 8). Therefore it is thought that the cross-link density also decreased with increasing MDS content in the TGAC/hybrid hardener system.

It is noteworthy that the appearance of the α'-relaxation peak in the tan δ curve for both DGEBA and TGAC modification indicates the presence of a phase-separated structure for the modified resin and corresponds to the morphology of the modified resin.

In the modification of DGEBA with low MW PMS, K_{IC} increased with decreasing cross-link density but K_{IC} for the high MW PMS (10 wt%)-modified resin decreased abruptly on addition of MDS (Fig. 1). The low MW PMS-modified resins had a two-phase structure, independent of PMS concentration and the hardener composition. On addition of 10 wt% of high MW PMS, the morphologies of the modified

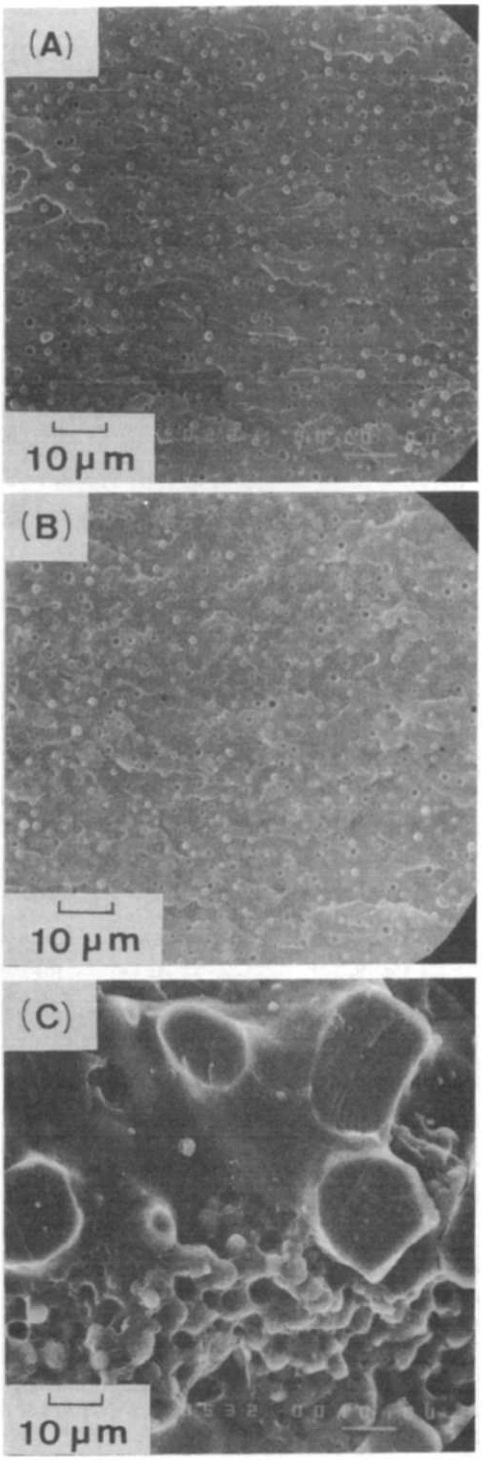


Fig. 13. SEMs of fracture surfaces for the cured TGAC resins modified with PMS. PMS ($\bar{M}_w$ 214,000): (A) 10 wt% addition, DDS/MDS 90:10 NH ratio; (B) 10 wt% addition, DDS/MDS 65:35 NH ratio; (C) 15 wt% addition, DDS/MDS 65:35 NH ratio.

---

*The cross-link density, ρ, was calculated from the equilibrium storage modulus, G', in the rubber region over the α-relaxation temperature according to the following equation.

$$\rho = G'/\phi RT$$

where ϕ, R and T are the front factor (usually equal to unit), the gas constant and the absolute temperature in the rubber region, respectively.

Details of the experimental procedure for the cross-link density of the resins are given in Ref. [7].

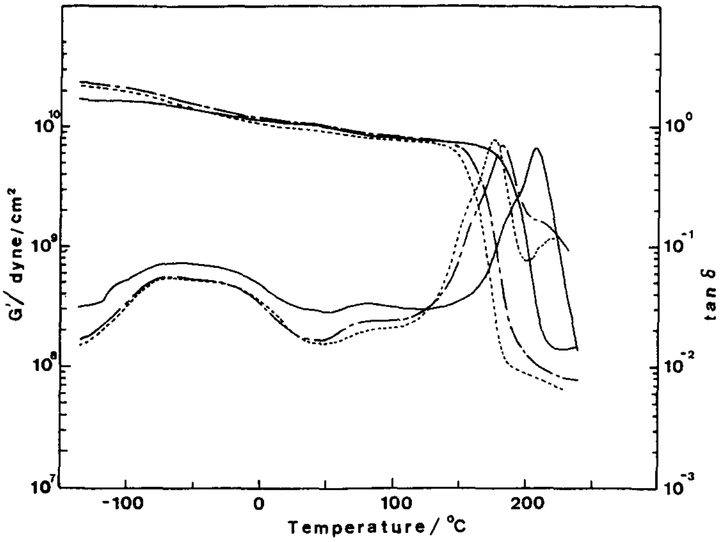


Fig. 14. Dynamic viscoelastic analysis for unmodified and PMS-modified DGEBA resins. PMS, $\bar{M}_w$ 214,000: ——, unmodified, DDS only; —-—, PMS 10 wt% addition, DDS/MDS 75:25 NH ratio; -----, PMS 10 wt% addition, DDS/MDS 65:35 NH ratio.

resins changed drastically; the DDS-cured resin had the cocontinuous phase morphology but the modified resin became a two-phase structure when using the hybrid hardener (DDS:MDS, 48/52 mol ratio, 65/35 NH ratio) [Fig. 11(A) and (D)]. The dependence of K_{IC} on the hardener composition was studied in detail for 10 wt% addition of high MW PMS (Fig. 3). K_{IC} for the unmodified DGEBA resin hardly changed with the hardener composition as reported previously [7]. K_{IC} for the modified DGEBA resins increased gradually on addition of up to 33 mol% of MDS (25 NH%) and then decreased abruptly, together with change in morphology. When using DDS only or the hybrid hardener of low MDS content, the modified resins had cocontinuous phase morphologies, but the morphology of the modified resin cured with the hybrid hardener of high MDS content (DDS:MDS, 65/35 NH ratio) had a two-phase structure. This result indicates that the PMS-rich phase changes from the cocontinuous phase to the two-phase separation structure with decrease in the cross-linked density of the DGEBA matrix before gelation or vitrification. The fracture behaviour corresponds to the morphology of the modified resin. K_{IC} for the modified DGEBA resin increased considerably for the cocontinuous phase structure.

PMS was also effective as a modifier for the TGAC/DDS system with highly cross-linked structure. On addition of 10 wt% of PMS, K_{IC} increased discontinuously according to the PMS MW (Fig. 5).

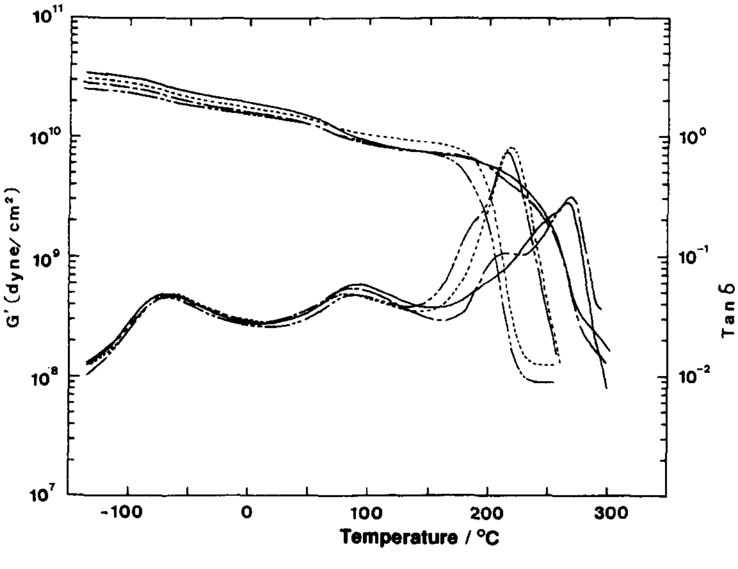


Fig. 15. Dynamic viscoelastic analysis for unmodified and PMS-modified TGAC resins. PMS, $\bar{M}_w$ 214,000: ——, unmodified, DDS only; —-—, PMS 10 wt% addition, DDS only; -----, unmodified DDS/MDS 65:35 NH ratio; —--—, PMS 10 wt% addition, DDS/MDS 65:35 NH ratio.

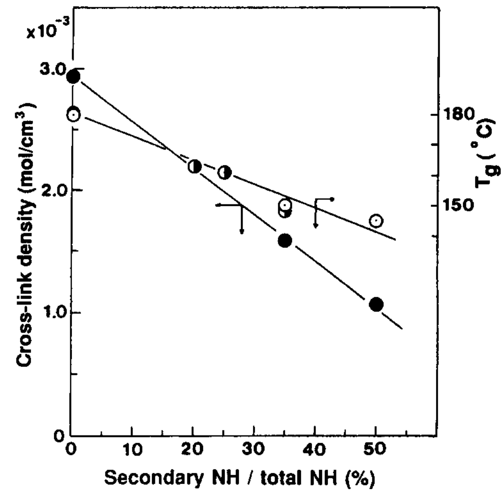


Fig. 16. Dependence of the cross-link density and T_g on the hybrid hardener composition in the DGEBA curing system. ●, Cross-link density for the unmodified resins; ⊙, T_g for the unmodified resins; ◑, T_g for the PMS (10 wt%)-modified resins.

The use of PMS with MW >200,000 led to a great increase in K_{IC}. This behaviour is similar to that in the DGEBA/DDS system [21] but the effectiveness of PMS in the former system is somewhat lower than in the latter. Morphologies of the modified resins also depended on PMS MW. When using 10 wt% of lower MW PMS (150,000), the modified resin had a two-phase structure and the higher MW PMS-modified resins had the cocontinuous phase structure [Fig. 12(A) and (B)]. In the TGAC/hybrid hardener system, inclusion of 10 wt% of high MW PMS led to a significant decrease in K_{IC} even for low MDS content (10 NH%) (Fig. 7). On addition of 15 wt% of PMS, K_{IC} increased slightly with increasing MDS content. This result can also be explained by the morphology of the modified resin. The high MW PMS (10 wt%)-modified resins have two-phase morphologies when using the hybrid hardener [Fig. 13(A) and (B)] but, on 15 wt% addition of high MW PMS, the modified resins have the cocontinuous phase morphology in the hybrid hardener system (DDS:MDS, 65:35 NH ratio) [Fig. 13(C)]. K_{IC} for the modified TGAC resin also increase based on the cocontinuous phase structure.

K_{IC} for the TGAC resins increased discontinuously with increase in high MW PMS concentration, depending on the crosslink density of the matrix (Fig. 9). In the TGAC/DDS system K_{IC} increased 70% on 10 wt% addition of PMS (214,000) and 100% on 15 wt% addition, together with change in morphology [Fig. 12(B)–(D)]. When using the hybrid hardener (DDS:MDS, 48:52 mol ratio), K_{IC} increased by 30% on 10 wt% addition of PMS (214,000) and 110% on 15 wt% PMS addition; the modified resin had a two-phase structure in the former and the cocontinuous structure in the latter [Fig. 13(B) and (C)]. It is noteworthy that K_{IC} for the modified resin increased even in the highly cross-link matrix such as the TGAC/DDS system.

In every case for the present modification system, the toughness of epoxy resin could be improved significantly because of the cocontinuous structure of the modified resins. The results indicate that toughening could be achieved by the absorption of fractural energy due to ductile drawing and tearing of the PMS-rich continuous phase and that a toughening mechanism based on the two-phase separation structure would not be important. The former mechanisms would be similar to that in the modification of epoxies with engineering thermoplastics such as poly(etherimide)s [13, 15] and poly(ether ketone)s [18].

The drawback in the PMS modification is the decrease in flexural strength. In the previous paper, solvent-etched fracture surfaces were obtained by SEMs to examine the interfacial adhesion between the PMS-rich phase and the epoxy matrix; the PMS-rich phase was clearly removed by etching THF in both two-phase and cocontinuous morphologies [21]; therefore there is no chemical interfacial adhesion. The decrease in flexural strength would be based on insufficient interfacial adhesion between the matrix and the PMS-rich phase. It is thought that this deficiency could be overcome by introducing functional groups into the modifier.

Engineering thermoplastics have high T_gs because of their rigid structures. PMS has also high T_g because of retardation of molecular motion of the main chains by the bulky side chains. One of the 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 the epoxies during modification with the thermoplastics. PMS used in this study is soluble in the epoxy resin without using solvent. The effectiveness of PMS as modifier could be explained by its structural similarity to PEI; the polar imide units in PEI and PMS would play an important role in the physical interfacial adhesion between the epoxy matrix and the thermoplastics.

In the DGEBA/DDS system, T_g for the modified resins are almost equal to that for the unmodified DGEBA resin. In the TGAC modification, T_gs for the modified DDS-cured resins are lower than that for the unmodified TGAC resin. In every case, T_g for the modified resin decreased with increasing MDS content of the hybrid hardener.

In conclusion, PMS is an interesting and effective modifier for improving the toughness of epoxy resins such as the TGAC/DDS matrix with highly cross-linked structure. Two toughening mechanisms appear to operate in the present modification system depending on PMS MW and concentration, and the structure of the matrix; one mechanism is due to a two phase separation structure and the other mechanism to the cocontinuous phase morphology. The most effective modification for the cured epoxy resins can be achieved in the latter case.

Acknowledgement—The authors thank Dr Shinji Takeda (Hitachi Chemical Industrial Co., Ltd) for obtaining the dynamic viscoelastic data.

REFERENCES

1. A. F. Yee and R. A. Pearson. *J. Mater. Sci.* **21,** 2462, 2475 (1986) and references cited therein.
2. R. A. Pearson and A. F. Yee. *J. Mater. Sci.* **24,** 2571 (1989).
3. M. Tomoi, J. Yamazaki, H. Akada and H. Kakiuchi. *Angew. Makromolek. Chem.* **163,** 63 (1988).
4. T. Iijima, M. Tomoi, J. Yamasaki and H. Kakiuchi. *Eur. Polym. J.* **26,** 145 (1990).
5. T. Iijima, M. Tomoi, A. Suzuki and H. Kakiuchi. *Eur. Polym. J.* **27,** 851 (1991).
6. T. Iijima, T. Horiba and M. Tomoi. *Eur. Polym. J.* **27,** 1231 (1991).
7. T. Iijima, N. Yoshioka and M. Tomoi. *Eur. Polym. J.* **28,** 573 (1992); in this paper the numerical values of the cross-link density were incorrect; the factor 10^{-3} was omitted.
8. C. B. Bucknall and I. K. Partridge. *Polymer* **24,** 639 (1983).
9. R. S. Raghara. *J. Polym. Sci., Part B, Polym. Phys.* **25,** 1017 (1987).
10. R. S. Raghara. *J. Polym. Sci., Part B, Polym. Phys.* **26,** 65 (1988).
11. J. H. Hedrick, I. Yilgor, G. L. Wilkens and J. E. McGrath. *Polym. Bull.* **13,** 201 (1985).
12. J. H. Hedrick, I. Yilgor, M. Jurek, J. C. Hedrick, G. L. Wilkens and J. E. McGrath. *Polymer* **32,** 2020 (1991).
13. C. B. Bucknall and A. H. Gilbert. *Polymer* **30,** 213 (1989).
14. R. S. Bauer, H. D. Stenzenberger and W. Romer. *Int. SAMPE symp.* **34,** 899 (1989).
15. A. H. Gilbert and C. B. Bucknall. *Makromolek. Chem. Macromolec. Symp.* **45,** 289 (1991).
16. A. Murakami, D. Saunders, K. Oishi, T. Yoshiki, M. Saito, O. Watanabe and M. Takezawa. *Nippon Setchaku Gakkaishi* **27,** 364 (1991).
17. B. Z. Jang, J. Y. Lian, L. R. Hwang and W. K. Shih. *J. Reinf. Plast.* **8,** 312 (1989).
18. T. Iijima, T. Tochimoto and M. Tomoi. *J. appl. Polym. Sci.* **43,** 1685 (1991).
19. A. F. Yee and R. A. Pearson. *Polym. Mater. Sci. Engng* **63,** 311 (1990).
20. T. Iijima, T. Tochimoto, M. Tomoi and H. Kakiuchi. *J. appl. Polym. Sci.* **43,** 463 (1991).
21. T. Iijima, N. Arai, K. Takematsu, W. Fukuda and M. Tomoi. *Eur. Polym. J.* **28,** 1539 (1992).
22. T. Iijima, K. Sato, W. Fukuda and M. Tomoi. *J. appl. Polym. Sci.* (in press).
23. J. M. Barrales-Rienda, J. I. Campa and J. G. Ramos. *J. Macromolec. Sci., Chem.* **A11,** 267 (1977).