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EFFECT OF CROSS-LINK DENSITY ON MODIFICATION OF EPOXY RESINS WITH REACTIVE ACRYLIC ELASTOMERS

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Abstract—The effect of cross-link density on the toughness of modified resins was investigated for modification of epoxy resins with acrylic elastomers with pendant epoxy groups. The elastomers were prepared by terpolymerization of butyl acrylate (BA), glycidyl methacrylate (GMA) and acrylonitrile (AN). The cross-link density of the epoxy matrix was controlled using hybrid hardeners composed of *p,p'*-diaminodiphenyl sulphone (DDS) as a primary diamine and *p,p'*-(*N,N'*-dimethyl)-diaminodiphenyl sulphone (MDS) as a secondary diamine. The terpolymers were effective as modifiers for toughening of difunctional epoxy resins (bisphenol A diglycidyl ether). The addition of 20 wt% of the terpolymer (62 mol% BA, 25 mol% GMA and 13 mol% AN, $\bar{M}_n$ 7900) led to a 100% increase in the fractural toughness of the resin cured with the hybrid hardener (DDS/MDS, 48:52 mol ratio, 65:35 NH ratio). The lower the cross-link density, the larger was the fracture toughness and the lower was the glass transition temperature. On the other hand, the terpolymers were less effective in the modification of trifunctional epoxy resins of higher cross-link density (triglycidyl aminocresol) even when using the hybrid hardener (DDS/MDS, 48:52 mol ratio). Both modified systems afforded cured resins with two-phase morphologies. The toughening mechanism is discussed in terms of the morphological and dynamic mechanical behaviours of the modified epoxy resin systems. It is concluded that the ductility of the epoxy matrix contributes greatly to toughening of epoxy resins with acrylic elastomers.

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, being brittle and having 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]. In previous papers, epoxide-containing acrylic rubbers, prepared by copolymerization of n-butyl acrylate (BA) with vinylbenzyl glycidyl ether (VBGE) [3] or terpolymerization of BA, VBGE and styrene (St) or acrylonitrile (AN) [4], have been reported as decreasing the brittleness of *p,p'*-diaminodiphenyl sulphone (DDS)-cured epoxy resins. Glycidyl (meth)acrylates (GA or GMA) were also used as more convenient monomers containing pendant epoxy groups, in place of VBGE. BA/GA or BA/GMA copolymers and BA/GMA/AN or BA/GMA/St terpolymers were prepared and used as effective modifiers [5, 6].

Most of the modification with reactive elastomers have been carried out using difunctional epoxy resins such as diglycidyl ether of bisphenol A. On the other hand, in the modification of highly cross-linked epoxy matrix, reactive rubbers such as CTBN have been reported as ineffective modifiers [1]. DDS-cured tetraglycidyl diaminodiphenylmethane (TGDDM) resin with highly cross-linked structure is often used as a structural adhesive and a matrix resin for high performance composites. Recently, Rezaifard *et al.* reported that graft copolymers of natural rubber and poly(methyl methacrylate) were effective in the modification of TGDDM [7]. It is interesting how the reactive acrylate elastomers containing pendant epoxy groups would behave in the modification of multifunctional epoxy resins.

There have been few studies on the relation between the toughening of epoxy resins and the cross-link density of the epoxy matrix. Kinloch *et al.* [8] varied the molecular weight between cross-links in the CTBN-modified epoxy resins cured with piperidine by changing the cure time and temperature. The fracture energy, G_{IC}, increased when the cross-link density was decreased. Pearson and Yee [9] studied the toughness of CTBN-modified bisphenol A diglycidyl ethers with various epoxy equivalent weights, using DDS as hardener. A decrease in the cross-link density produced a small increase in G_{IC} for the unmodified resin and a significant increase in G_{IC} for the modified resin. The cross-link density was controlled by the curing conditions in the former study and by the molecular weight of the starting epoxy resins in the latter. The cross-link density of epoxy matrix was also regulated by a curing agent in the modification of fluorene-containing epoxy resins, materials with a rigid planar structure [10], where the epoxy resin was cured with a combination of fluorene type primary and secondary diamines of similar structure and the decreased cross-link density also resulted in considerable increase in G_{IC} of cured resins.

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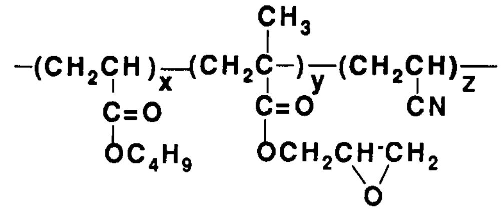
This paper reports the effect of cross-link density on the modification of DDS-cured epoxy resins with acrylic elastomers prepared by radical terpolymerization of BA, GMA and AN. The cross-link density of the epoxy matrix was controlled using MDS, a secondary diamine. The effect of the cross-link density on the toughness of the cured epoxy resin was examined.



EXPERIMENTAL PROCEDURES

Materials

Epoxy resins were the liquid bisphenol A type epoxy resin (DGEBA) [AER 331, Asahi Chemical Industrial Co., epoxy equivalent weight (EEW) 191] and the liquid aminocresol type trifunctional epoxy resin (TGAC) (ELM-100, Sumitomo Chemical Industrial Co., EEW 113). DDS and MDS were used as curing agents. Elastomers were prepared by radical terpolymerization as reported previously [4–6]. Other reagents were used as received.

Measurements

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 elastomers and cured resins were measured by differential scanning calorimetry (Shimadzu DSC 41 M type) at a heating rate of 10°/min except for cured TGAC resins. The T_g for the TGAC resins was obtained by thermal mechanical analysis (Shimadzu TMA 40 M type) at a heating rate of 5°/min. Scanning electron micrographs were taken with a JEOL JSM 35 instrument using failed specimens in the K_{IC} tests. Dynamic viscoelastic analysis was performed with a Rheometrics RDS-II type (Rheometrics Co.) between −130°–250° at a heating rate of 5°/min at frequency of 1 Hz. 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 equation [11]

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

where ϕ, R and T are the front factor (usually equal to unity), the gas constant and the absolute temperature in the rubber region, respectively. $(T_g + 40)°$ is often used as the T value in the equilibrium storage modulus [12], but the storage modulus at $(T_g + 30)°$ was better as the plateau region in the present curing system except for the unmodified DGEBA/DDS resin, for which $(T_g + 25)°$ was used.

Preparation of MDS

MDS was prepared according to the scheme.

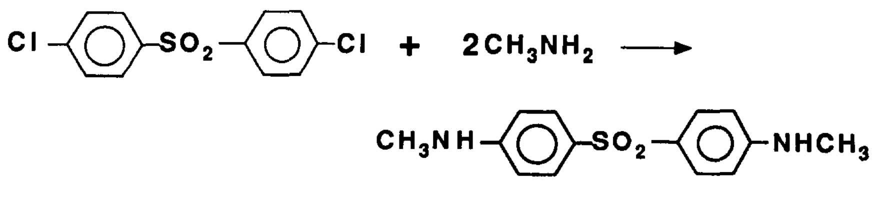


Table 1. Characterization of terpolymers

No.	BA	GMA	AN	$\bar{M}_n$ [a]	$\bar{M}_w/\bar{M}_n$ [a]	EEW[b] (g/eq)	T_g[c] (°C)
	Terpolymer composition						
I[d]	62	25	13	7900	1.61	488	−32
II	66	22	12	7300	1.69	561	−32
III[d]	57.5	24.5	18	7200	1.66	482	−30

[a] By GPC.
[b] Epoxy equivalent weight. Determined by HCl/dioxane method.
[c] By DSC.
[d] See Ref. [6].

A 200 ml stainless pressure bottle was charged with dichlorodiphenyl sulphone (33.8 g, 0.117 mol), potassium carbonate (18.7 g, 0.186 mol) and *N*-methylpyrolidone (NMP) (70 ml). After the solids had been dissolved with stirring, anhydrous chilled (−78°) monomethylamine (18.3 g, 0.590 mol) was added. The reaction mixtures were kept at 160° for 3 days. After the reaction was over, the resulting salts were removed by filtration and washed with methanol. The filtrate was poured into water (5 l.) to remove NMP. The crude product was separated as a white solid, washed with hot water and dried *in vacuo* at 80° for 15 hr. The crude product (29.3 g, 90%) was purified by recrystallization from toluene/dioxane mixture (400 ml/200 ml). Yield 28.3 g (87%), m.p. 174–176° (Ref. [13] 170–172°).

It is noteworthy that the preparation process of MDS in this study differs from the published method [13], in which MDS was prepared in aqueous solution.

Curing procedure

A mixture of the epoxy resin and the terpolymer was heated at 120° to homogenize, and the curing agents, DDS and MDS, were added to the mixture, which was kept at 120° for about 1 hr to dissolve DDS and MDS. The resulting clean mixture was poured into a silicon mould preheated at 100°. The curing conditions were 120° for 1 hr followed by 180° for 5 hr. The amount (wt%) of terpolymers used was calculated according to the amount of epoxy resins, DGEBA and/or TGAC. The curing agents (DDS and MDS) were used stoichiometrically to the total epoxy content of both the epoxy resins and the terpolymers.

RESULTS

Mechanical and thermal properties of modified epoxy resins

Table 1 reports some characteristic properties of the acrylic terpolymers used here. The elastomers were designed from the results of the previous papers [3–6], considering the compatibility of elastomers with the epoxy matrix: elastomers containing >86 mol% of BA units had low compatibility with the epoxy matrix, and modification with 20 wt% addition of the copolymer of higher epoxy content (45 mol% of VBGE units) resulted in a homogeneous structure for the cured resin, where no increase in the fracture toughness was observed. In this paper, elastomers **I**, **II** and **III** were used as equivalent modifiers. For

Table 2. Mechanical and thermal properties of cured DGEBA resins[a]

	Entry No.						
	1	2	3	4	5	6	7
Composition (wt ratio)							
DGEBA/terpolymer **I**	100/0	100/0	100/0	80/20	80/20	80/20	80/20
Hardener composition							
DDS/MDS (mol ratio)	100/0	48/52	33/67	100/0	67/33	48/52	33/67
(NH ratio)	100/0	65/35	50/50	100/0	80/20	65/35	50/50
Flexural strength (kgf/mm^2)	15.5 ± 0.6	15.5 ± 0.3	14.5 ± 0.4	12.5 ± 0.7	11.5 ± 0.6	12.0 ± 0.5	12.1 ± 0.3
Flexural modulus (kgf/mm^2)	299 ± 6	293 ± 10	263 ± 12	263 ± 8	255 ± 13	254 ± 7	255 ± 5
n[b]	7	9	5	6	6	7	8
K_{IC} (MN m$^{-3/2}$)	0.70 ± 0.01	0.71 ± 0.04	0.71 ± 0.04	0.94 ± 0.05	1.08 ± 0.06	1.22 ± 0.08	1.38 ± 0.03
n[b]	7	6	7	6	4	7	5
T_g[c] (C)	180 (200)[d]	150	145	179	155	138	126

[a] The ±x values show standard deviations.
[b] Number of specimens.
[c] By DSC.
[d] By TMA.

example, on addition of 20 wt% of the terpolymers, the K_{IC} values (MNm$^{-3/2}$) for the **I**-, **II**- and **III**-modified resins were 0.94, 0.95 and 0.89, respectively, in the DGEBA/DDS curing system. The results for the modification with terpolymers **I** or **III** have been reported previously [6].

The cross-link density of the epoxy matrix was controlled using MDS, an aromatic secondary diamine, as a chain extender. The cross-link density of the matrix was dependent on the hardener compositions (DDS and MDS) as described later in the dynamic viscoelastic behaviour of the cured resins. Table 2 shows the dependence of the mechanical properties of the cured resins on the hardener compositions in the DGEBA system. The flexural strength and modulus for the unmodified DGEBA resin decreased to some extent when using 67 mol% of MDS (Entry No. 3), compared to the DGEBA/DDS system (Entry No. 1). The K_{IC} values for unmodified resins hardly changed with the hardener compositions. On addition of 20 wt% of terpolymer **I**, K_{IC} increased with increasing MDS content at slight expense of mechanical properties. In the curing system of DDS/MDS (33/67 mol ratio), K_{IC} for the **I** (20 wt%)-modified resin (Entry No. 7) increased 100%, compared to that for the DDS-cured unmodified resin (Entry No. 1). T_gs of the cured resins decreased with the increased MDS content.

Figures 1 and 2 show the mechanical properties of the cured DGEBA resins as a function of the elastomer concentration; the results for the DDS-cured resins have been reported previously [6]. The flexural strength and moduli for the modified resins decreased gradually with increase in the elastomer concentration (Fig. 1). The fractural behaviours of the modified resins depended on the hardener composition (Fig. 2). K_{IC} for the DDS-cured resins increased gradually and tended to level off with increasing elastomer **I** concentration. On addition of 25 wt% of **I**, K_{IC} of the modified resin increased 35%. On the other hand, the use of the hybrid hardener (DDS/MDS 48/52 mol ratio, 65/35 NH ratio) led to a linear increase of K_{IC} with increase in elastomer **II** content. K_{IC} of the **II** (25 wt%)-modified resin showed a 90% increase, compared to the unmodified resin cured with the same hybrid hardener. Figure 3 shows the dependence of T_g on the elastomer content. T_g decreased slightly with increase in the elastomer content.

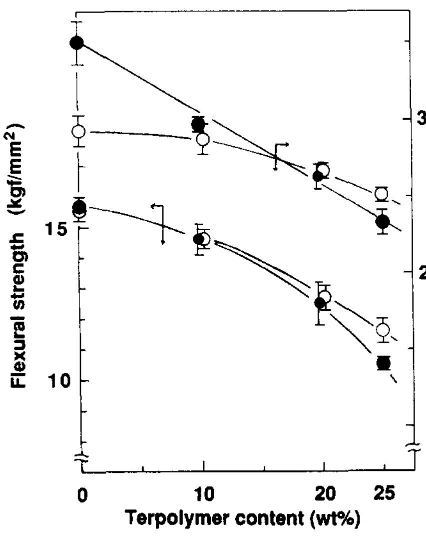


Fig. 1. Flexural strength and modulus of the elastomer-modified DGEBA resins as functions of the elastomer concentration. ○, Elastomer **II**; DDS/MDS 48:52 mol ratio; ●, elastomer **I**; DDS only.

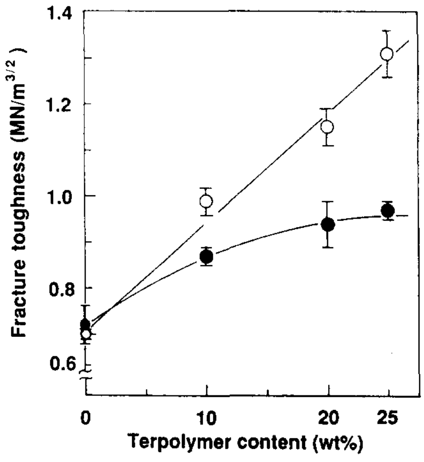


Fig. 2. Dependence of fracture toughness for modified DGEBA resins on the elastomer concentration. ○, Elastomer **II**; DDS/MDS 48:52 mol ratio; ●, elastomer **I**; DDS only.

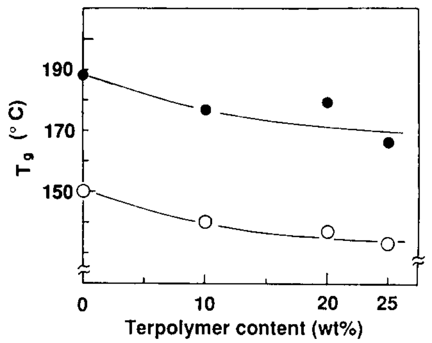


Fig. 3. Glass transition temperatures of the cured DGEBA resin. ○, Elastomer **II**; DDS/MDS 48:52 mol ratio; ●, elastomer **I**; DDS only.

Table 3 shows the results for modification in the epoxy blend containing the trifunctional epoxy resin (TGAC). In a unmodified DGEBA/TGAC (80:20 wt ratio) blend cured with DDS (Entry No. 1 in Table 3), the flexural strength was comparable, the flexural modulus and T_g were larger, and K_{IC} hardly differed from those in the DGEDA/DDS curing system (Entry No. 1 in Table 2). The extent of improvement in the toughening of the epoxy blend cured with DDS (Entry Nos 1 and 2 in Table 3) was comparable to the fracture behaviour in the modification of the DGEBA/DDS system (Entry Nos 1 and 4 in Table 2). T_g for the modified epoxy blend/DDS resin (Entry No. 2 in Table 3) increased *ca* 20° over that for the modified DGEBA/DDS resin (Entry No. 4 in Table 2). In the modification of the epoxy blend, K_{IC} for the resin cured with the hybrid hardener (Entry No. 4 in Table 3) was larger than that for the DDS-cured resin (Entry No. 2 in Table 3).

Table 3 also shows the results in the modification of TGAC. The flexural strength and modulus for the DDS-cured TGAC resin were larger than those for the DGEBA/DDS resin system. The fractural behaviour in the TGAC/DDS system was quite different from that in the DGEBA or DGEBA/TGAC resins. There was no improvement in the brittleness of the modified TGAC/DDS resin. In the use of the hybrid hardener, K_{IC} for the TGAC resin increased slightly. T_g was measured by thermal mechanical analysis, as DSC could not be used because of the exothermal peak. In general it is difficult to cure fully tri- or tetrafunctional epoxies because of the network steric restriction for the epoxy group [14]. In this study, boron trifluoride monoethylamine complex was also used as accelerator in the curing of the TGAC/DDS system, but the exothermal peak was still observed in the DSC analysis. T_g (237°) for the TGAC/DDS resin exceeded that (200°) for the DDS-cured DGEBA resin as obtained by TMA. T_g for TGAC resins decreased on modification with the elastomers. The use of MDS also led to a decrease in T_g for the unmodified and modified resins.

Dynamic viscoelastic analysis of the modified resins

Dynamic viscoelastic analysis can give information on the micro-structure of cured resins. Figures 4 and 5 show the storage moduli, G', and tan δ for the unmodified and **I**-modified DGEBA resins, respectively. In both curing systems, the peak position of the α-relaxation in the tan δ curves shifted towards lower temperature with increasing MDS content in the hardener, compared to the dynamic viscoelastic behaviour for the DDS-cured epoxy resin. The storage moduli above the α-transition temperature also decreased with increasing MDS content. The storage modulus in the glassy state hardly changed up to 48 mol% of MDS content and then decreased. The apparent cross-link density, ρ, was calculated based on the storage modulus, G', in the rubbery region at higher temperature, T, than the α-relaxation according to the theory of rubber elasticity. Table 4 shows the apparent cross-link density of the cured resins. Figure 6 shows plots of the cross-link density vs the hardener composition in both the unmodified and modified resins. The cross-link density of the cured resin decreased with increasing MDS content. It is noteworthy that the acetone insoluble fraction was obtained in 57 wt% in the cured resin with only MDS (Soxhlet extraction conditions; 8.5 days at reflux temperature).

Morphologies of the cured resins

Figure 7 shows the scanning electron micrographs (SEMs) of the cured resins. Morphological results for the cured resins are collected in Table 5. The unmodified resins were transparent and had only one phase, independent of the hardener compositions. The morphology of the unmodified DGEBA resin cured with DDS/MDS (33:67 mol ratio) was very

Table 3. Mechanical and thermal properties of cured epoxy resins[a]

	Entry No.							
	1	2	3	4	5	6	7	8
Composition (wt ratio)								
D/T/M[b]	80/20/0	64/16/20	80/20/0	64/16/20	0/100/0	0/80/20	0/100/0	0/80/20
Hardener composition								
DDS/MDS (mol ratio)	100/0	100/0	48/52	48/52	100/0	100/0	48/52	48/52
Flexural strength (kgf/mm^2)	15.5 ± 0.8	11.1 ± 0.4	16.7 ± 0.4	13.0 ± 0.2	16.4 ± 0.4	12.5 ± 0.4	18.4 ± 0.4	14.3 ± 1.5
Flexural modulus (kgf/mm^2)	334 ± 7	253 ± 12	315 ± 12	272 ± 3	431 ± 13	342 ± 13	399 ± 11	348 ± 7
n[c]	6	7	7	5	6	4	4	6
K_{IC} (MNm$^{-3/2}$)	0.67 ± 0.04	0.90 ± 0.05	0.68 ± 0.01	1.02 ± 0.03	0.61 ± 0.04	0.60 ± 0.05	0.60 ± 0.06	0.71 ± 0.09
n[c]	7	5	5	6	5	5	5	4
T_g[d] (°C)	198	195	145	140	237[e]	221[e]	199[e]	177[e]

[a] The ±x values show standard deviations.
[b] D, DGEBA; T, TGAC; M, modifier. Use of terpolymer **II** except for No. 8, where terpolymer **III** was used.
[c] Number of specimens.
[d] By DSC.
[e] By TMA.

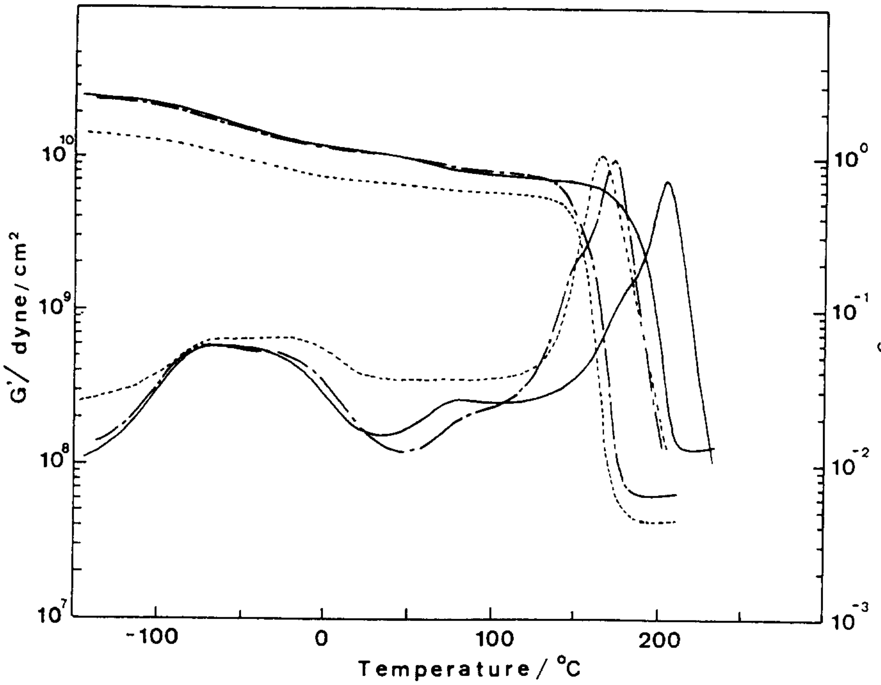


Fig. 4. Dynamic viscoelastic analysis for unmodified cured DGEBA resin. DDS/MDS mol ratio: ——, 100:0; — - —, 48:52; -----, 33:67.

similar to that of the DDS-cured unmodified resin [Fig. 7(A)]. The elastomer-modified resins had two-phase morphology with the elastomer-rich phase forming dispersed spherical particles in the epoxy-rich matrix. Morphologies of the elastomer I (20 wt%)-modified resin were unimodal in the hybrid curing system and hardly changed up to addition of 52 mol% of MDS, compared to the I-modified resin cured with DDS [Fig. 7(B)]. When using 67 mol% of MDS, the size distribution of the particles became bimodal [Fig. 7(C)]. The volume fraction of the dispersed particles for the I-modified resins was nearly equal to or larger than the weight fraction of the elastomer added. In the hybrid hardener system (DDS/MDS, 48/52 mol ratio), the volume fraction of the dispersed particle increased with increasing ter-

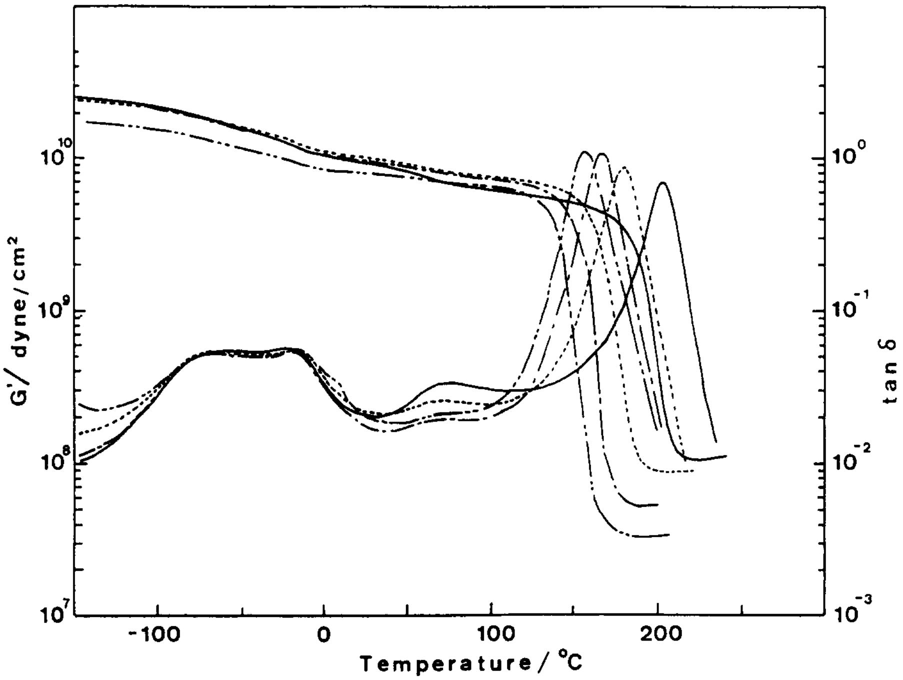


Fig. 5. Dynamic viscoelastic analysis for cured DGEBA resin modified with 20 wt% of I. DDS/MDS mol ratio: ——, 100:0; -----, 67:33; — - —, 48:52; — - - —, 33:67.

Table 4. The cross-link densities of cured DGEBA resins

Resin composition							
DGEBA/terpolymer (wt ratio)	100/0	100/0	100/0	80/20	80/20	80/20	80/20
Hardener composition							
DDS/MDS (mol ratio)	100/0	48/52	33/67	100/0	67/33	48/52	33/67
(NH ratio)	100/0	65/35	50/50	100/0	80/20	65/35	50/50
T_g(°C)[a]	203	172	167	200	181	165	159
G' (dyne/cm^2)·10^{-7} [b]	12.27[c]	6.25	4.23	10.47	8.40	4.93	3.17
ρ (mol/cm^2)	2.95	1.58	1.08	2.51	2.09	1.27	0.825

[a] By dynamic viscoelastic analysis.

[b] At $T = T_g + 30°$.

[c] At $T = T_g + 25°$.

polymer **II** concentration up to 25 wt% and was larger than the weight fraction of the terpolymer, but the particle sizes hardly changed.

The unmodified DGEBA/TGAC blends and TGAC resins were transparent and had one phase. Morphologies of the modified DGEBA/TGAC blends were similar to those for the modified DGEBA resins (Fig. 8 and Table 5). In the modified TGAC resin, the size distribution of the particles was bimodal independent of the hardener compositions (Fig. 9).

DISCUSSION

The storage modulus in the plateau region over the α-relaxation is related to the cross-link density of the cured resins. It has been reported that short chain networks of cured resins might show non-Gaussian character in the rubber region of higher storage modulus ($G' > 10^7$ Pa) and extensibility of network would be restricted, and then the rubber elasticity theory might hold no longer [9, 15]. But LeMay and Kelly show that the rubber modulus of highly cross-linked epoxies can be used as a practical means to predict the average network chain molecular weight of the short chain DGEBA/DDS systems [16]. Then the cross-link density was calculated from the storage modulus above T_g (Table 4). Increase in the MDS content of the hybrid hardener led to decrease in the storage modulus. This result indicates that the cross-link density can be controlled systematically by using MDS, a secondary diamine, as shown in Fig. 6.

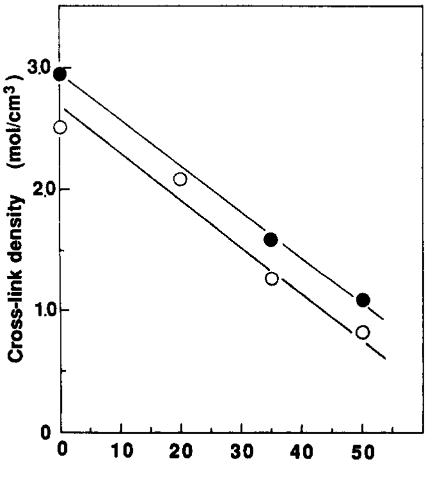


Fig. 6. Relationships between the cross-link density and MDS content. ○, Elastomer I 20 wt% addition; ●, unmodified resin.

The reactive acrylic elastomers with pendant epoxy groups were more effective as modifiers in the use of the DDS/MDS hybrid hardener than the DDS curing system in the modification of both DGEBA and DGEBA/TGAC mixed resins. Figure 10 shows the dependence of mechanical properties on the cross-link density. Flexural strength for the unmodified resins decreased slightly, dependent on the cross-link density. Flexural strength for the modified DGEBA resin decreased compared to that for the unmodified resin. The flexural properties for modified resins were approximately independent of the cross-link density. On the other hand, the fractural behaviour depended on the curing systems to a greater extent. K_{IC} values for unmodified resins were independent of the cross-linking density, but those for the modified DGEBA resins increased linearly with decreasing cross-link density. K_{IC} for the **I** (20 wt%)-modified resin increased 100% when using DDS/MDS 50/50 (NH ratio), compared to that for the unmodified DGEBA resin. T_g decreased with decrease in the cross-link density of the cured resins (Fig. 11).

The morphology of the modified resin cured with the hybrid hardener of higher MDS content (DDS/MDS, 33/67 mol ratio, 50:50 NH ratio) changed considerably compared with the modified resins cured with DDS or the hybrid hardener of lower MDS content. The morphology of the former resin was bimodal and consisted of smaller (2.5 ± 1.0 μm) and larger (9.5 ± 4.0 μm) particles. The smaller particle sizes are similar to those in the latter system (Table 5). These results suggest that the dispersed particles can coagulate into larger particles in the lower cross-linked matrix before gelation or vitrification. There are claims that a bimodal distribution of particle sizes is beneficial in rubber-modified epoxy resins [17] but, in the modification of DGEBA, K_{IC} increases with decrease in the cross-link density, independent of morphologies such as the elastomer particle distribution (Fig. 10). Recently, Pearson and Yee also reported that a bimodal particle size distribution did not result in a greater increase in fracture toughness in the modification of epoxy resins with rubbers [18]. Morphologies of modified resins were also bimodal in both TGAC/DDS and TGAC/hybrid hardener systems. The particle sizes are 2.7 ± 1.2 μm for smaller particles and 9.5 ± 4.5 μm for larger ones in the TGAC/DDS resin. The morphology (3.4 ± 1.1 μm and 9.4 ± 3.6 μm) of the hybrid hardener-cured TGAC resin is similar to that of the TGAC/DDS system. It is noteworthy that the morphology of the

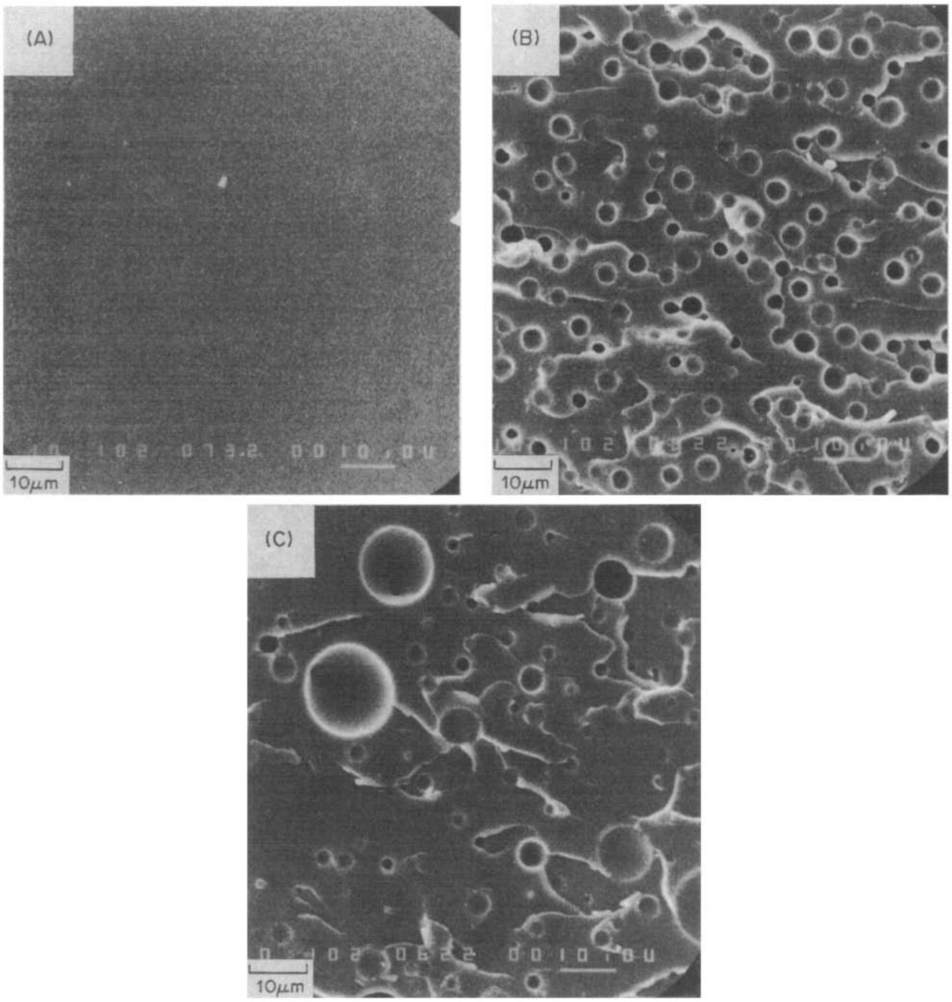


Fig. 7. SEMs of fracture surfaces for the cured resins. (A) Unmodified DGEBA resin cured with the hybrid hardener (DDS/MDS, 33:67 mol ratio). (B) **I** (20 wt%)-modified DGEBA resin, DDS/MDS, 48:52 mol ratio. (C) **I** (20 wt%)-modified resin, DDS/MDS, 33:67 mol ratio.

Table 5. Morphological results

Resin composition DGEBA/terpolymer	Curing agent[a] DDS/MDS	Feed terpolymer[b] weight fraction	D^c	V_f^d	N[e]
100/0	100/0	0	—	0	0
DEGBA/I series					
80/20	100/0	0.156	2.5 ± 1.2	0.142	2.5
80/20	67/33	0.148	3.3 ± 0.9	0.192	2.1
80/20	48/52	0.142	3.1 ± 0.9	0.197	2.5
80/20	33/67	0.137	3.7 ± 3.0^f	0.152	0.9
DGEBA/II series					
80/20	100/0	0.156	4.0 ± 0.8	0.192	1.3
90/10	48/52	0.072	2.5 ± 0.6	0.087	1.7
80/20	48/52	0.143	3.2 ± 0.8	0.183	2.2
75/25	48/52	0.255	3.1 ± 0.7	0.255	3.3
DGEBA/TGAC/II or III series					
64/16/20[g]	100/0	0.152	4.0 ± 0.8	0.181	1.3
64/16/20[g]	48/52	0.138	3.8 ± 1.0	0.128	1.1
0/80/20[g]	100/0	0.137	4.5 ± 3.7^f	0.165	0.6
0/80/20[h]	48/52	0.120	6.1 ± 3.8^f	0.150	0.35

[a] Mol·ratio.
[b] Based on the total resin.
[c] Average particle diameter in μm. The $\pm x$ values show standard deviations.
[d] Volume fraction of dispersed particle.
[e] Number of particles/100 μm.
[f] Bimodal distribution.
[g] Terpolymer **II**.
[h] Terpolymer **III**.

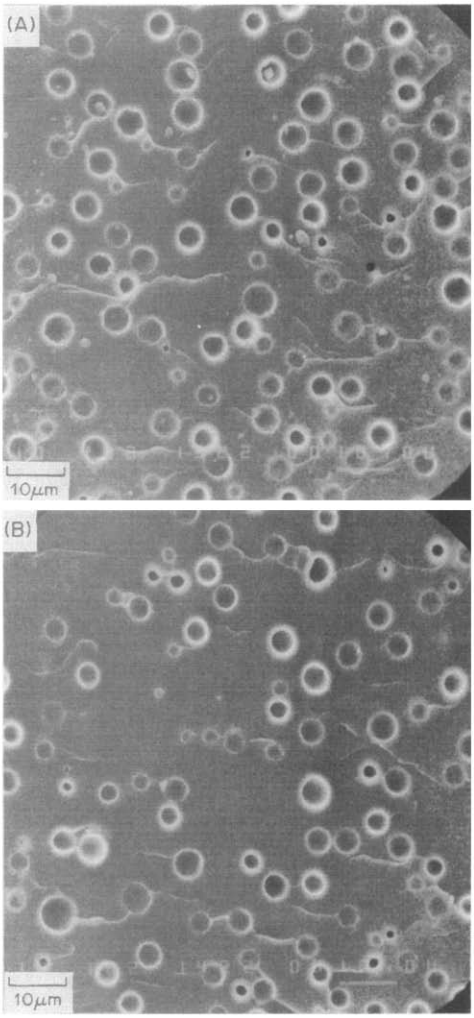


Fig. 8. SEMs of fracture surfaces for the modified DGEBA/TGAC blends. DGEBA/TGAC, 80/20 wt ratio; **II** 20 wt% addition. (A) DDS only; (B) DDS/MDS, 48:52 mol ratio.

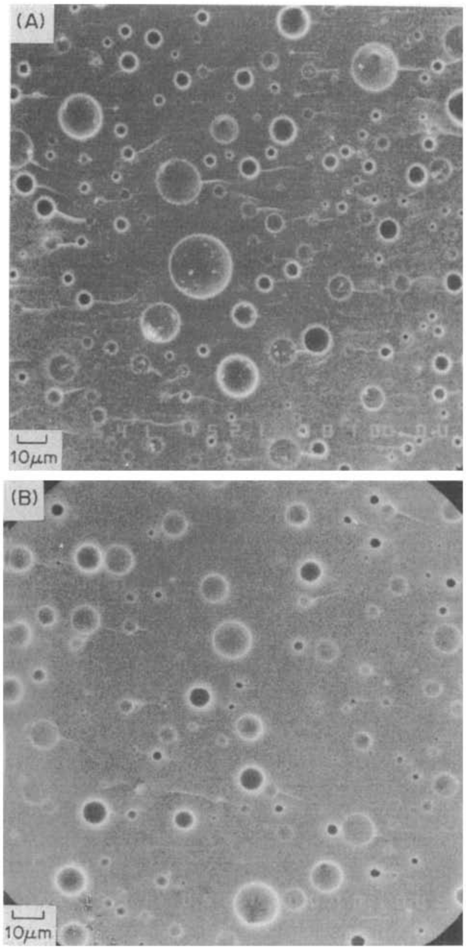


Fig. 9. SEMs of fracture surfaces for the modified TGAC resins. (A) **II** 20 wt% addition, DDS only; (B) **III** 20 wt% addition, DDS/MDS, 48:52 mol ratio.

modified TGAC resin is also similar to that of the above modified DGEBA resin cured with the hybrid hardener of higher MDS content: however, the process of phase-separation in the modification of TGAC might be different from that in the modified DGEBA resins, considering the more highly cross-linked matrix of the former resin [19]. The terpolymers were less effective in the TGAC curing system, though the morphology of the modified TGAC resin was similar to that of the modified DGEBA resin cured with the hybrid hardener of higher MDS content.

The difference in the extent of toughening between the DGEBA and TGAC systems is instructive when considering the toughening mechanism in the modification with the present reactive acrylic elastomers.

It is well-known that toughening epoxy resins by elastomers should satisfy two requirements, viz. the existence of microphase separated structure and interfacial bonding between two uncompatibilized phases. Morphologies of the present elastomer-modified resins have two-phase structure, and elastomer-rich particles dispersed in both epoxy matrices. The interfacial adhesion is due to covalent bonding between the epoxy matrix and the dispersed particles.

Toughening in the modification with elastomers could be attained by dissipating the fracture energy because of the following various process. When hydrostatic pressures are applied to specimens with an initial crack, particles in front of the crack tip act as stress concentrators; they cavitate and interact with each other. Such interaction between particles induces shear band near the crack and the crack tip is blunted by plastic shear deformation of the matrix. When the hydrostatic force increases, the crack propagate unstably, particles are elongated and torn, and crack deflection and crack bifurcation are brought about. There are small differences in morphology between the modified DGEBA and TGAC resins, but the fracture behaviours are quite different. Morphological results indicate that the elastomer particles would act as stress concentrators in the TGAC/DDS curing system as well as in the modified DGEBA/DDS resins. In the former modification, however, the plastic deformation at fracture would be induced to a smaller extent owing to higher cross-

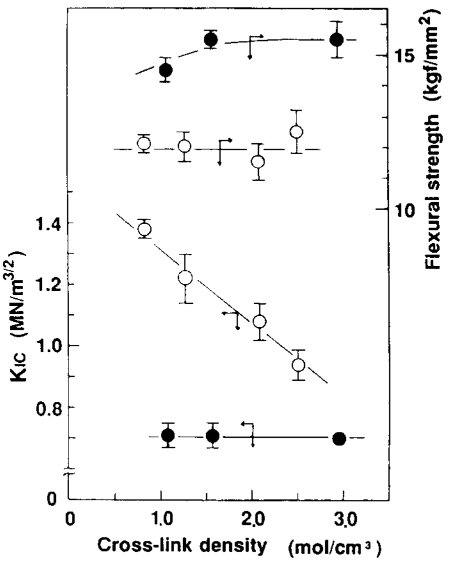


Fig. 10. Dependences of mechanical properties for cured resins on cross-link density. ○, Elastomer **II**-modified DGEBA resins; ●, unmodified DGEBA resins.

linked structure of the matrix, compared to the latter. The fact that there is no increase in K_{IC} in the former system could be explained by difference in the extent of plastic deformation near the crack tip. These results indicate that the contribution of the plastic deformation due to the ductility of the matrix to toughening of the epoxy resin is one of the most important factors in the modification with the present reactive elastomers. The importance of ductility of the matrix has been reported in the modification with reactive rubbers such as CTBN: CTBN is effective in the piperidine-cured DGEBA resin, the lower cross-linking system, but far less effective in the DGEBA/DDS resin, the higher one [1, 9]. The present terpolymers are still effective in the DGEBA and DGEBA/TGAC blend/DDS systems, but less effective in the TGAC resin.

In conclusion, the reactive acrylic elastomers with pendant epoxy groups were more effective as modifiers for the DDS/MDS hybrid hardener than the DDS curing system for the modification of both DGEBA and DGEBA/TGAC blend. In the curing system of DDS/MDS (33/67 mol ratio), K_{IC} for the terpolymer **I** (20 wt%)-modified resin increased 100%, compared to that for the unmodified DDS-cured resin. K_{IC} of the terpolymer **II** (25 wt%)-modified resin showed a 90% increase, compared to the unmodified resin. The terpolymers were less effective for the higher cross-linking TGAC curing system. These results indicate that ductility of the matrix is necessary to some extent to decrease the brittleness of epoxy resins in the modification with reactive elastomers or rubbers.

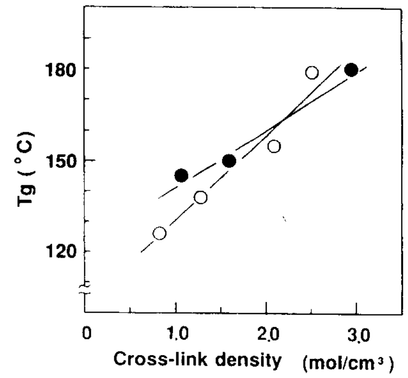


Fig. 11. T_g dependences on cross-link density. ○, Elastomer **II**-modified DGEBA resins; ●, unmodified DGEBA resins.

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REFERENCES

1. A. F. Yee and R. A. Pearson. *J. Mater. Sci.* **21**, 2462, 2475 (1986) and references cited therein.
2. J. H. Hedrick, I. Yilgor, G. L. Wilkens and J. E. McGrath. *Polym. Bull.* **13**, 201 (1985); C. B. Bucknal and A. H. Gilbert. *Polymer* **30**, 213 (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. A. Rezaifard, K. Dodd and J. Barton. *Polym. Mater. Sci. Engng* **63**, 201 (1990).
8. A. J. Kinloch, C. A. Finch and S. Hashemi. *Polym. Commun.* **28**, 322 (1987).
9. R. A. Pearson and A. F. Yee. *J. Mater. Sci.* **24**, 2571 (1989).
10. G. B. Portelli, W. J. Schultz, R. C. Jordan and S. C. Hackett. *Compos. Polym.* **2**, 381 (1989).
11. L. E. Nielsen. *Mechanical Properties of Polymers and Composites*, (Jpn. Transl.), p. 110. Kagakudohjin, Japan (1982).
12. K. Hasegawa, A. Fukuda, S. Tonogai and H. Horiuchi. *Kobunshi Ronbunshi* **40**, 321 (1983); M. Ogata, T. Kawata and N. Kinjo. *Kobunshi Ronbunshi* **44**, 193 (1987).
13. I. Dobas and J. Eichler. *Collect. Czech. Chem. Commun.* **38**, 3279 (1973).
14. T. Iijima, H. Hiraoka, M. Tomoi and H. Kakiuchi. *J. appl. Polym. Sci.* **41**, 2301 (1990).
15. G. Levita, S. De. Petris, A. Marchetti and A. Lazzeri. *J. Mater. Sci.* **26**, 2348 (1991).
16. J. D. LeMay and F. N. Kelley. *Adv. Polym. Sci.* **78**, 115 (1986).
17. W. D. Bascom, R. Y. Ting, R. J. Moulton, C. K. Riew and A. R. Siebelt. *J. Mater. Sci.* **16**, 2657 (1981).
18. R. A. Pearson and A. F. Yee. *J. Mater. Sci.* **26**, 3828 (1991).
19. K. Yamanaka, Y. Takagi and T. Inoue. *Polymer* **30**, 1839 (1989).