Eur. Polym. J. Vol. 27, No. 9, pp. 851–858, 1991
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0014-3057/91 \$3.00 + 0.00

TOUGHENING OF EPOXY RESINS BY MODIFICATION WITH REACTIVE ELASTOMERS COMPOSED OF BUTYL ACRYLATE AND GLYCIDYL (METH)ACRYLATE

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(Received 2 January 1991; in revised form 21 March 1991)

Abstract—Acrylic elastomers with pendant epoxy groups were used to reduce the brittleness of bisphenol-A diglycidyl ether epoxy resin cured with *p,p'*-diaminodiphenyl sulphone. The elastomers were prepared by copolymerization of butyl acrylate (BA) with glycidyl acrylate (GA) or methacrylate. These copolymers were effective for toughening of the epoxy resin system. The addition of 20 wt% of copolymer (74 mol% BA and 26 mol% GA) led to 60% increase in the fracture toughness of the cured resin at slight expense of its mechanical properties. The glass transition temperatures of cured resins were comparable to that of the parent epoxy resin. The toughening mechanism is discussed in terms of the morphological and dynamic viscoelastic behaviour of the modified epoxy resin system.

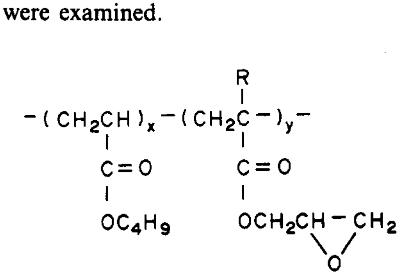
INTRODUCTION

Epoxy resins are one of the most important thermosetting polymers and have wide use as structural adhesives and matrix resins for fiber composites, but their cured resins have one drawback; they are brittle and have poor resistance to crack propagation. The toughnesss of epoxy resins has been increased by blending with reactive liquid rubbers [1] or terminally functionalized engineering thermoplastics [2–6]. In previous papers epoxide-containing acrylic rubbers, prepared by copolymerization of *n*-butyl acrylate (BA) with vinylbenzyl glycidyl ether (VBGE) [7] or terpolymerization of BA, VBGE and styrene (St) or acrylonitrile (AN) [8], have been reported as decreasing the brittleness of epoxy resin. It has also been reported that the microphase separation of cured resin and its interfacial binding are necessary to improve the toughness of epoxy resin by modification with elastomers [7]. In these copolymer system, the compatibility of elastomers with epoxy resins depended on the composition of elastomers, and the interfacial binding was done by the covalent bonding of epoxy resins with pendant epoxy groups of elastomers. The BA–VBGE–St terpolymers were most effective among the above elastomers as modifiers for epoxy resins. The addition of 30 wt% of the terpolymer, composed of 62 mol% BA, 22 mol% VBGE and 16 mol% St units, led to 130% increase in the fracture toughness, K_{IC}, of the cured resin at slight expense of its mechanical properties. It is noteworthy that elastomers containing more than 86 mol% of BA units had low compatibility with epoxy matrix and that modification with elastomer of higher epoxy content (55 mol% BA and 45 mol% VBGE) resulted in a homogeneous structure of cured resin, where an increase in the fracture toughness of cured resins was hardly observed owing to the rigid structure. The elastomer without the pendant epoxy group (70 mol% BA and 30 mol% vinylbenzyl 2-methoxyethyl ether) was an inefficient modifier because of the absence of the interfacial bonding, though the cured resin has a two-phase morphology comparable to that modified with a BA–VBGE elastomer (74 mol% BA and 26 mol% VBGE), an effective modifier.

VBGE is an interesting and important compound containing both epoxy and vinyl units, but it must be prepared via three steps starting with chloromethylstyrene (a mixture of *m*- and *p*-isomers, 6:4 mol ratio). Therefore we decided to prepare acrylic elastomers using glycidyl (meth)acrylate (GA or GMA), more convenient epoxides, in place of VBGE and study their effectiveness as modifiers for epoxy resins.

This paper reports the modification of *p,p'*-diaminodiphenyl sulphone-cured epoxy resins (diglycidyl ether of bisphenol A, DGEBA) with acrylic elastomers (I or II), prepared by copolymerization of BA with GA or GMA.

The effects of the amount and composition of added copolymer on the toughness of the cured epoxy resin were examined.



$$-(\mathrm{CH_2}\underset{\substack{|\\ \mathrm{C=O}\\ |\\ \mathrm{OC_4H_9}}}{\mathrm{CH}})_x-(\mathrm{CH_2}\overset{\substack{\mathrm{R}\\ |}}{\underset{\substack{|\\ \mathrm{C=O}\\ |\\ \mathrm{OCH_2CH-CH_2}\\ \diagdown\mathrm{O}\diagup}}{\mathrm{C}}}-)_y-$$

(I) R=H (II) R=CH_3

Scheme 1

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Table 1. Preparation and characterization of acrylic elastomers

	Feed composition			Yield	Copolymer composition							
No.	BA	GA	(GMA)	%	BA	GA	(GMA)	M_n^a 10^{-3}	M_w/M_n^a	EEW[b]	T_g^c (°C)	SP[d] $(cal/cm^3)^{1/2}$
Ia	65	35		71	74	26		4.1	3.69	486	−39	10.11
Ib	70	30		76	72	28		8.7	4.88	457	−46	10.14
Ic	75	25		66	77	23		8.3	2.42	549	—	10.06
IIa	85		(15)	36	81		(19)	17.0	1.73	679	—	9.94
IIb	70		(30)	64	73		(27)	20.0	1.70	490	−34	10.01
IIc	85		(15)	40	75		(25)	7.7	1.56	532	—	10.00

[a] By GPC.

[b] Determined by the HCl/dioxane method.

[c] By DSC.

[d] Calculated by Fedors' method. The SP value for the parent epoxy resin is 10.60.

EXPERIMENTAL PROCEDURES

Materials

The epoxy resin was the liquid bisphenol-A type epoxy resin (DGEBA) [Epikote 828, Shell Chemical Co., epoxy equivalent weight (EEW) 190]. *p,p'*-Diaminodiphenyl sulphone (DDS) was used as curing agent without further purification. BA, GA and GMA were purified in the usual manner. Other reagents were used as received.

Measurements

Molecular weights of copolymers were determined by gel permeation chromatography (Shimadzu LC-5A instrument) using polySt standards. Epoxy groups in polymers were determined by the HCl/dioxane method [9]. Glass transition temperatures of both copolymers and cured resins were measured by differential scanning calorimetry (Shimadzu DSC 41M type). Mechanical properties of cured resins were measured with a Shimadzu S-500 universal testing machine. Tensile strength and modulus (JIS K7113) of cured resins were determined using dumb-bell specimens at a cross head speed of 1 mm/min. Flexural strength and modulus (JIS K7203) were obtained at a cross head speed of 2 mm/min. Fracture toughness (K_{IC}, ASTM E-399) was measured in a three-point bent geometry at a cross head speed of 1 mm/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° and 250° at a heating speed of 5°/min at a frequency of 1 Hz.

Preparation of copolymers

A flask was charged with a mixture of monomers (total content, 1 mol), toluene (300 ml) and azobisisobutyronitrile (AIBN, 0.03 mol). The flask was purged with N_2 for 0.5 hr and a N_2 atmosphere was maintained throughout the polymerization. The polymerization mixture was stirred at 70° for 20 hr. Copolymers were isolated using hexane as precipitant and purified twice by reprecipitation with tetrahydrofuran/hexane. The liquid copolymers were dried *in vacuo* at 60°. The compositions of BA/GA(GMA) copolymers were obtained from epoxy content.

It is noteworthy that a large amount of toluene (5 l) was used in place of the usual amount (300 ml) to control the molecular weight of the BA–GMA copolymer (Entry No **IIc** in Table 1).

Curing procedure

A mixture of the epoxy resin and copolymer was heated at 80° for about 1 hr to homogenize and degas, and the curing agent, DDS, was added to the mixture, which was kept at 120° to dissolve DDS. The resulting mixture was then poured into a silicon mould preheated at 100° and cured at 120° for 1 hr followed by post-cured at 180° for 5 hr. The amount (wt%) of copolymer used was calculated based on the amount of the epoxy resin, DGEBA. The curing agent was used stoichiometrically to the total epoxy content of both the epoxy resin and the copolymers.

RESULTS

Characterization of copolymers

Table 1 reports some characteristic properties of acrylic copolymers, **I** and **II**. The molecular weight distribution of **Ib** was bimodal by GPC. The molecular weight of **IIc** was controlled using a large amount of toluene as a solvent. The copolymers in Table 1 were designed from the results of the previous paper [7], considering the compatibility of elastomers with epoxy matrix: elastomers containing >86 mol% of BA units had low compatibility with epoxy matrix, and modification with 20 wt% addition of the copolymer of the higher epoxy content (45 mol% of VBGE units) resulted in the homogeneous structure of cured resin.

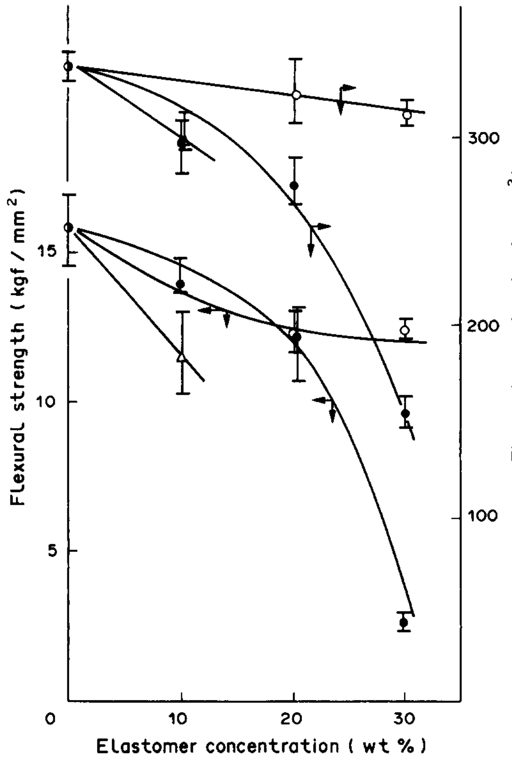

Fig. 1. Flexural strength and modulus of copolymer-modified epoxy resins as function of copolymer concentration and structure. ◑, Control; ○, **Ia**(BA 74 mol%, M_n 4100); ●, **Ib**(BA 72 mol%, M_n 8700); △, **Ic**(BA 77 mol%, M_n 8300).

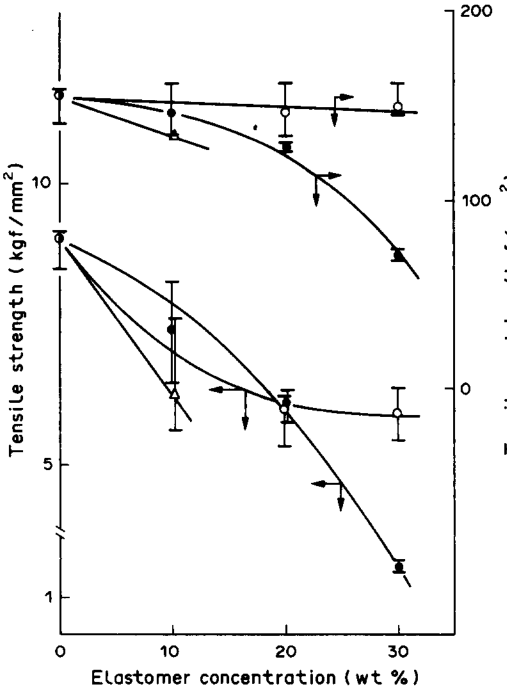

Fig. 2. Tensile strength and modulus of copolymer-modified epoxy resins as function of copolymer concentration and structure. ◐, Control; ○, **Ia**(BA 74 mol%, M_n 4100); ●, **Ib**(BA 72 mol%, M_n 8700); △, **Ic**(BA 77 mol%, M_n 8300).

Mechanical and thermal properties of modified epoxy resins

Figures 1–6 show the mechanical properties of the cured resins as a function of concentration of the elastomers. The cured parent epoxy resin was transparent but the elastomer modified cured resins were opaque.

The flexural strength and modulus for the resin modified with BA–GA copolymer I depended on the concentration and molecular weight of the copolymer (Fig. 1). The use of low molecular weight **Ia** (BA 74 mol%, $\bar{M}_n$ 4100) resulted in a gradual decrease in the flexural strength and modulus, compared to those of the parent epoxy resin. In spite of the similar composition of the copolymers, the addition of

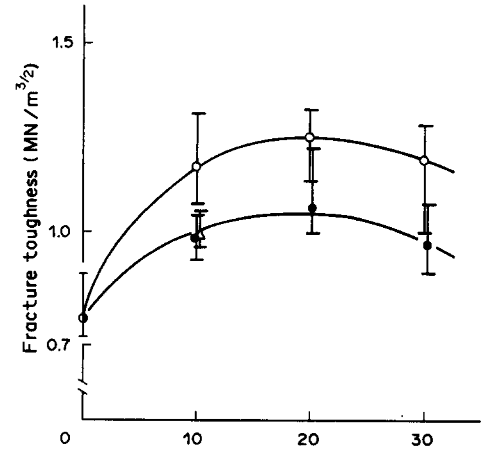

Fig. 3. Dependence of fracture toughness (K_{IC}) for modified resins on copolymer concentration and structure. ◐, Control; ○, **Ia**(BA 74 mol%, M_n 4100); ●, **Ib**(BA 72 mol%, M_n 8700); △, **Ic**(BA 77 mol%, M_n 8300).

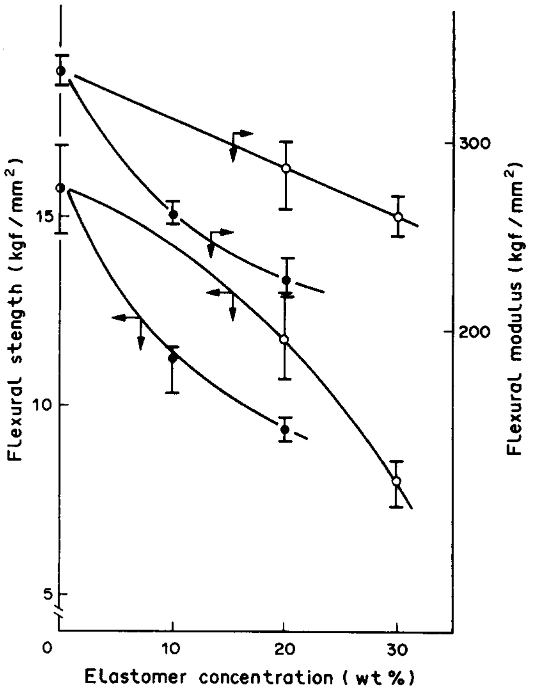

Fig. 4. Flexural strength and modulus of copolymer-modified epoxy resins as function of copolymer concentration and structure. ◐, Control; ●, **IIa**(BA 81 mol%, M_n 17,000); ○, **IIb**(BA 73 mol%, M_n 20,000).

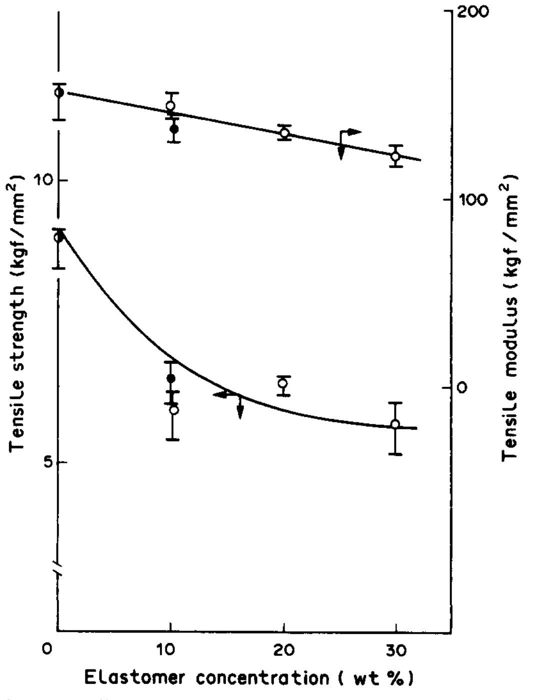

Fig. 5. Tensile strength and modulus of copolymer-modified epoxy resins as function of copolymer concentration and structure. ◐, Control; ●, **IIa**(BA 81 mol%, M_n 17,000); ○, **IIb**(BA 73 mol%, M_n 20,000).

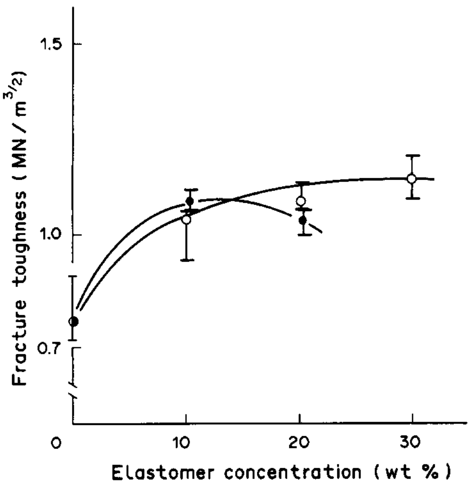

Fig. 6. Dependence of fracture toughness (K_{IC}) for modified resins on copolymer concentration and structure. ◑, Control; ●, **IIa**(BA 81 mol%, M_n 17,000); ○, **IIb**(BA 73 mol%, M_n 20,000).

30 wt% of higher molecular weight **Ib** (BA 72 mol%, $\bar{M}_n$ 8700) led to a larger decrease in flexural strength and modulus. The dependence of the tensile properties for the modified resins on the concentration and molecular weight of copolymer **I** were similar to those of the flexural properties (Fig. 2). The use of BA-rich copolymer **Ic** (BA 77 mol%, $\bar{M}_n$ 8300) tended to macroscopic separation. The cured resin could not be obtained owing to separation of sticky materials containing a large amount of **Ic** in the surface of the cured resin on 20 wt% addition. The fracture toughness (K_{IC}) of the modified resin also depended on the composition and molecular weight of the copolymers **I** (Fig. 3). In the modification with lower molecular weight **Ia**, the K_{IC} values increased with increasing copolymer content up to 20 wt% and then decreased slightly. On addition of 20 wt% of **Ia**, the K_{IC} increased 60% at slight expense of its mechanical properties. The use of higher molecular weight **Ib** in the modification led to an increase in K_{IC} to a smaller extent.

The flexural and tensile properties of the cured resins modified with the BA–GMA copolymers **II** decreased with an increase in the copolymer concentration (Figs 4 and 5). In the modification with **IIb** (BA 73 mol%, M_n 20,000) the flexural strength and modulus decreased gradually with increasing **IIb** content. The extent of decrease in flexural properties was larger in the cured resins modified with **IIa** (BA 81 mol%, M_n 17,000). The use of **IIc** (BA 75 mol%, M_n 7700) led to macrophase separation even on 15 wt% addition. In the modification with **IIa** the K_{IC} increased 40% on addition of 10 wt% of **IIa** and then decreased slightly (Fig. 6). The K_{IC} of the cured resin modified with **IIb** increased 40% with increasing copolymer content up to 20 wt% and then hardly changed. On addition of 10 wt% of **IIc** the K_{IC} increased 30%.

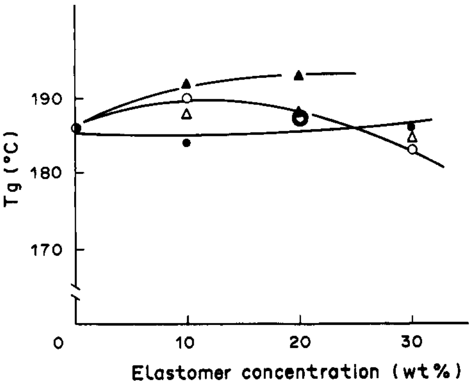

Fig. 7. Glass transition temperature (T_g) of the cured resins. ◑, Control; ○, **Ia**(BA 74 mol%, M_n 4100); ●, **Ib**(BA 72 mol%, M_n 8700); △, **IIa**(BA 81 mol%, M_n 17,000); ▲, **IIb**(BA 73 mol%, M_n 20,000).

Table 2. Morphological results

Resin composition DGEBA/copolymer	Feed copolymer[a] weight fraction	D^b	V_f^c	N^d
100/0	0	—	0	0
Ia series				
90/10	0.076	—	0	0
80/20	0.155	—	0	0
70/30	0.237	—	0	0
Ib series				
90/10	0.076	2.0 ± 1.0	0.027	0.8
80/20	0.157	2.0 ± 0.7	0.065	1.4
70/30	0.235	*ca* 25	—[e]	—[e]
Ic series				
90/10	0.077	8.6 ± 2.8	0.100	0.1
80/20[f]	0.160	—[e]	—[e]	—[e]
IIa series				
90/10	0.077	6.7 ± 3.4	0.078	0.1
80/20	0.155	6.6 ± 6.4	0.165	0.2
IIb series				
90/10	0.076	1.3 ± 0.6	0.030	4.3
80/20	0.158	3.9 ± 1.8	0.108	0.7
70/30	0.238	5.5 ± 2.8	0.132	0.4
IIc series				
90/10	0.077	2.8 ± 0.7	0.141	2.2
85/15[f]	0.117	—[e]	—[e]	—[e]

[a] Based on the total resin.

[b] Average particle diameter in μm. The ± x values show standard deviations.

[c] Volume fraction of dispersed particle.

[d] Number of particle/100 μm^2.

[e] Not obtained owing to the macrophase separation.

[f] Sticky materials containing a large amount of copolymers were separated in the surface of cured resins.

The glass transition temperatures, T_gs, of the cured resins were collected in Fig. 7. The T_g values for the modified resins with **I** or **II** were equal to or larger than T_g for the parent epoxy resin.

Morphology of the modified resins

Figure 8 shows the scanning electron micrographs (SEMs) of the cured resins. Morphological data for the cured resins in the modification with both **I** and **II** were collected in Table 2. The unmodified resin had only one phase, and the fracture surface was smooth and featureless as reported previously [7]. There was no domain in the fracture surface for the modified resin with the BA–GA copolymer **Ia** (BA 74 mol%, $\bar{M}_n$ 4100) up to a magnification of 10,000 [Figs 8(A) and (B)], but the fracture surface was rough, compared to that for the parent epoxy resin. In the modification with 10–20 wt% of **Ib** (BA 72 mol%, $\bar{M}_n$ 8700), two-phase morphology was seen with the epoxy-rich phase forming the continuous matrix and the elastomer-rich phase forming dispersed spherical particles [Fig. 8(C)]. The volume fraction, V_f, and number of the particles, N, increased with increasing **Ib** content up to 20 wt%, though the diameter, D, of the dispersed particles hardly changed. On addition of 30 wt% **Ib**, the modified cured resin led to the macro-phase separation. In the modification with 10 wt% of **Ic**, the particle size was far greater than for other modification systems because of its poor compatibility with the epoxy resin.

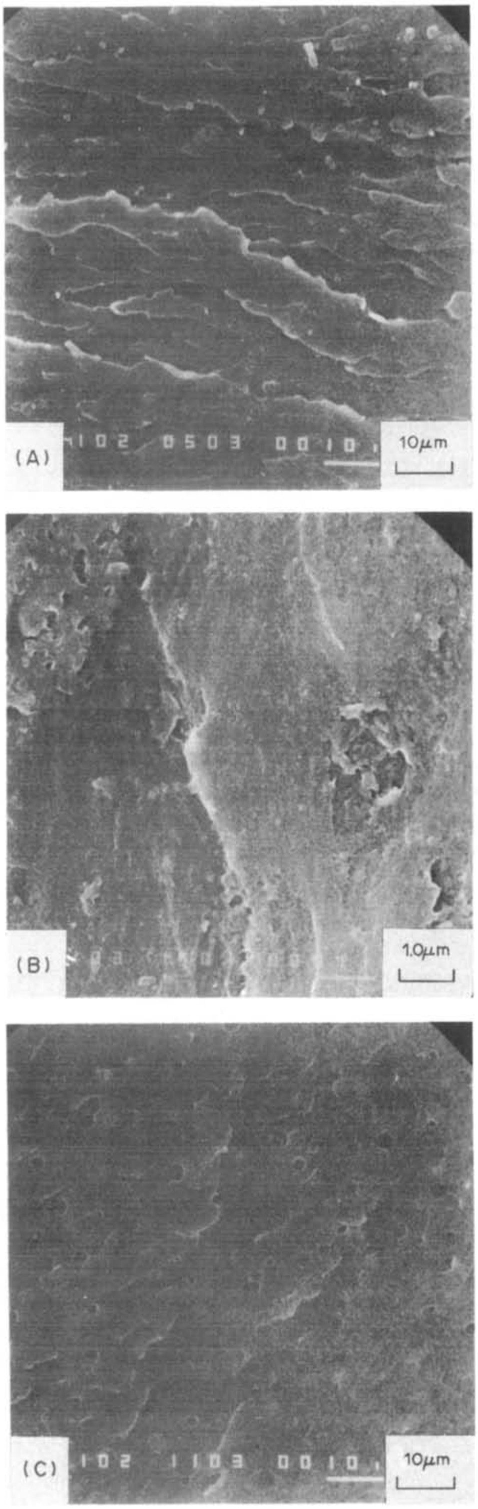

Fig. 8. SEMs of fracture surfaces for the cured resins modified with 20 wt% addition of the BA–GA copolymers **I**. (A) **Ia** (BA 74 mol%, M_n 4100), magnification 1000. (B) **Ia**, magnification 10,000. (C) **Ib** (BA, 72 mol%, M_n 8700).

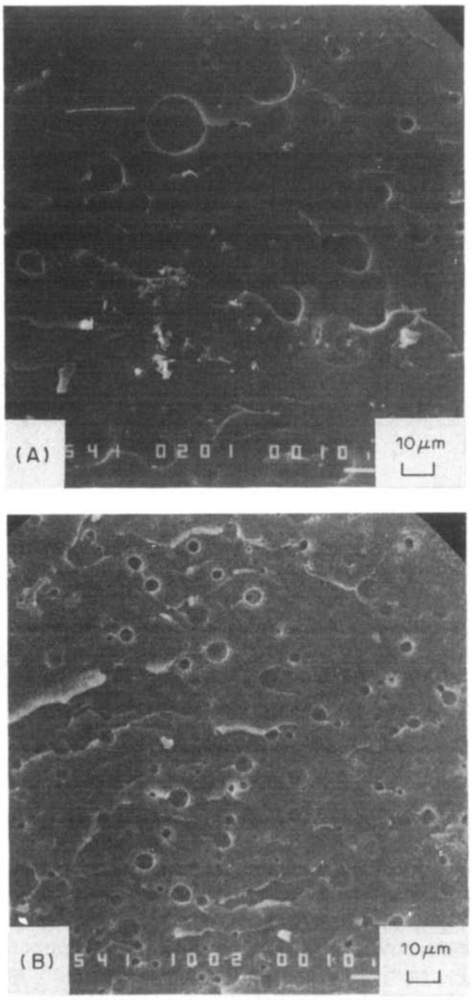

Fig. 9. SEMs of fracture surfaces for the cured resins modified with 20 wt% addition of the BA–GMA copolymers **II** in the magnification of 540. (A) **IIa**(BA 81 mol%, M_n 17,000). (B) **IIb** (BA 73 mol%, M_n 20,000).

The resins modified with BA–GMA elastomers **II** had two-phase morphology. The volume fraction of the dispersed particles for modification with **IIa** (BA 81 mol%, $\bar{M}_n$ 17,000) increased with increasing copolymer concentration, and was nearly equal to the weight fraction of the copolymer in the cured system [Fig. 9(A) and Table 2]. The particle size did not depend on the concentration of copolymer **IIa**. The particle size distribution on 20 wt% addition of **IIa** was larger than that in other modification systems. The size and volume fraction of particles for the modification with **IIb** (BA 73 mol%, $\bar{M}_n$ 20,000) increased with increase in the **IIb** content and were smaller than those for the cured resin modified with **IIa** [Fig. 9(B)]. The volume fraction of the particles was smaller than the weight fraction of the copolymer **IIb**. The volume fraction of the particle was larger than the weight fraction of **IIc** (BA 75 mol%, $\bar{M}_n$ 7300) in the modification with **IIc**.

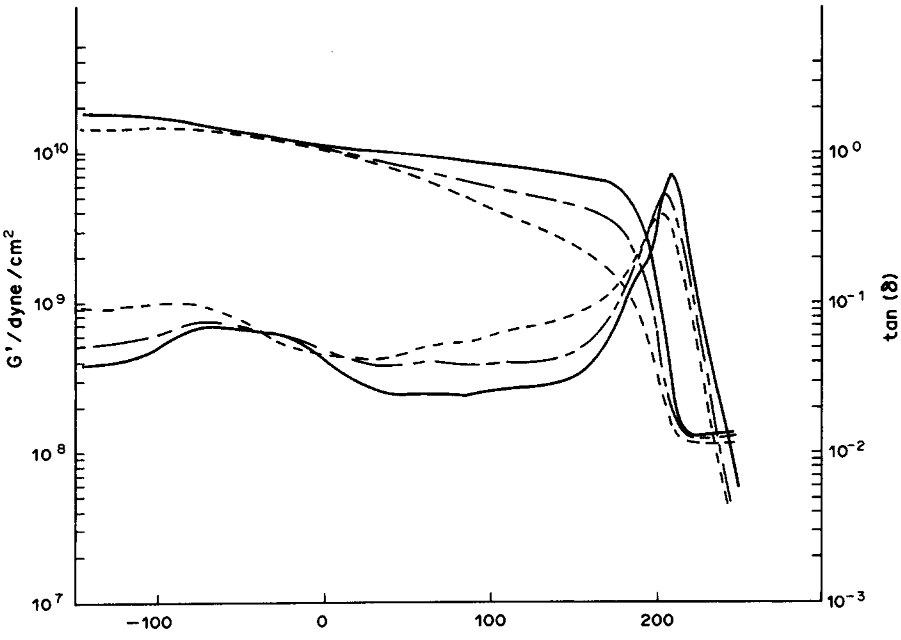

Fig. 10. Dynamic mechanical analysis for the cured resin. ——, Control; — — —, **Ia**, 20 wt% addition; ----, **Ia**, 30 wt% addition.

Dynamic viscoelastic analysis of the modified resins

Dynamic viscoelastic analysis can give information on the micro-structures of cured resins. Figure 10 shows the storage modulus, G', and tan δ curves for the resins modified with **Ia**. Increasing **Ia** content led to a gradual shift of the peak position of the α-relaxation in the tanδ curves towards lower temperature, a decrease in magnitude of the α-relaxation and the emergence of several broad relaxations at *ca* 50–150°. The storage modulus decreased with increasing **Ia** content.

The peak position and the magnitude of the α-relaxation peak in the tanδ curves for the resins modified with **IIb** hardly changed, but several new relaxation emerged at *ca*-20°, and 70–110° (Fig. 11). The storage modulus decreased gradually with increase in the copolymer concentration.

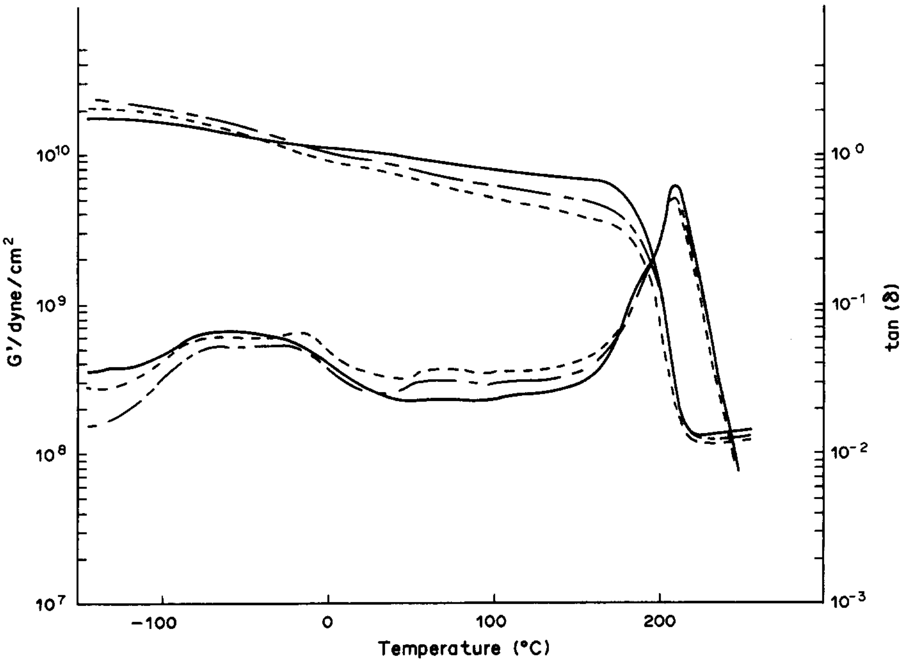

Fig. 11. Dynamic mechanical analysis for the cured resin. ——, Control; — — —, **IIb**, 20 wt% addition; ----, 30 wt% addition.

DISCUSSION

The reactive elastomers **I** and **II** with pendant epoxy groups were effective as modifiers for improving the toughness of the epoxy resin system. The control of copolymer composition is important, because copolymers having more than *ca* 85 mol% BA units result in macrophase separation and epoxy-rich copolymers are likely to dissolve into the epoxy matrix phase as reported previously [7]. The compositions of both BA–GA and BA–GMA copolymers were controlled according to such information (Table 1). Among the BA–GA copolymers, **Ic** (77 mol% BA, $\bar{M}_n$ 8300) tends to separate macroscopically as shown in morphological behaviour. This fact shows that copolymers having >BA 80 mol% units are unsuitable because of their poor compatibility in this modification. Among the BA–GMA copolymers, **IIc** (BA 75 mol%, $\bar{M}_n$ 7700) has poorer compatibility with the epoxy resin than other copolymers.

The toughening mechanism can be explained in terms of the morphological and dynamic mechanical behaviours.

In the modification with the BA–GA elastomers **I**, **Ia** is a most effective modifier in this study. The addition of 20 wt% of **Ia** led to 60% increase in K_{IC} of the cured resin at slight expense of its mechanical properties. The morphology of the fracture surface for the cured resin modified with **Ia** (BA 74 mol%, $\bar{M}_n$ 4100) shows an interesting result: there was no domain but the fracture was rough and ridged, based on the plastic deformation of the epoxy matrix itself prior to failure [Figs 8(A) and 8(B)]. Higher molecular weight **Ib** (BA 72 mol%, $\bar{M}_n$ 8700) resulted in microphase separated structure [Fig. 8(C)]. The volume fraction of the particle is smaller than the weight fraction of the copolymer added in the cured system. This result indicates that the elastomer **Ib** dissolves partially in the epoxy matrix phase. Morphological results in modifications with **Ia** and **Ib** of similar composition indicate that the compatibility of the BA–GA copolymers depends on their molecular weight. The elastomer **Ic** ($\bar{M}_n$ 8300) containing 77 mol% BA units has poorer compatibility with the epoxy resin than **Ib** (72 mol% BA, $\bar{M}_n$ 8700) with similar molecular weight. The composition dependence of compatibility with the epoxy resin might be explained in terms of the solubility parameters (SP) of the elastomers (see Table 1).

In the dynamic viscoelastic analysis for the **Ia**-modified resin (Fig. 10), the α-relaxation peak in the tanδ curve shifted gradually toward lower temperature and became broader with increasing **Ia** content, compared to the parent epoxy resin. Several new relaxations appeared in the region *ca* 50–150° but no peak based on the added elastomer was observed at *ca* −40°. The broadness of the α-relaxation and the presence of new relaxations can be attributed to the formation of a matrix phase containing both the parent epoxy resin and dissolved **Ia** in various amounts. This result shows high compatibility between the epoxy resin and **Ia**. These dynamic viscoelastic results correspond to the morphological results and the toughness of the cured resins. It is well known that the toughening of epoxy resins is based on the microphase-separated structure of the cured resin in the modification with reactive elastomers such as carboxyl-terminated butadiene–acrylonitrile rubber (CTBN) [1]: elastomer particles with diameter of a few microns were dispered in the epoxy matrix in the more effective modification system. The modification system with elastomer **Ia** may be a special case perhaps because of high compatibility of **Ia** with the epoxy resin. It is interesting that the K_{IC} values increase in spite of the homogeneous structure of the cured resins. It is thought that the toughness of the epoxy resin in the modification with **Ia** would be based on the plastic deformation of the epoxy matrix near the crack tip prior to failure. In the previous paper [7] the modified resin with the BA–VBGE elastomer of higher epoxy content (45 mol% VBGE) has a homogeneous structure, where an increase in the fracture toughness of cured resin was hardly observed. This effect may be explained by the rigid structure of the cured resin in the system with the BA–VBGE copolymer as modifier, owing to both strong interfacial covalent bonding via pendant epoxy units of higher content and poor elastic properties (T_g, −24°) of the added BA–VBGE copolymer. The BA–GA elastomer is more flexible (T_g, −39°) than the BA–VBGE elastomer. The use of the BA–GA elastomer would lead to an increase in the ductility of the epoxy matrix.

For modification with the BA–GMA elastomers **II**, **IIb** (BA 73 mol%, $\bar{M}_n$ 20,000) is more effective than **IIa** (BA 81 mol%, $\bar{M}_n$ 17,000). On addition of 20 wt% of **IIb**, K_{IC} increased 40% at slight expense of mechanical properties. The resins modified with elastomers **II** have two-phase morphology (Fig. 9). The morphology of the fracture surface for the cured resins modified with **IIa** shows that the particle diameter hardly changed with increase in the elastomer content, and that the volume fraction of the particle was equal to the weight fraction of the charged elastomer content. These morphological results indicate that elastomer **IIa** does not dissolve in the epoxy matrix. The particle size of the cured resin modified with **IIb** was less than that with **IIa**. The volume fraction of particle for the former modification was also smaller than for the latter: the elastomer **IIb** dissolves partially in the epoxy matrix. These morphological characteristics correspond to the results from dynamic viscoelastic analysis. The dynamic mechanical results show that the α-relaxation peak position and shape hardly changed with increasing **IIb** content, and that a new relaxation emerged at *ca* −20° (Fig. 11). These results indicate the occurrence of phase separation to some extent. Further, the emergence of several new relaxation in the range *ca* 50°–110° is due to intermixing of the epoxy and the elastomer in various composition. The toughening of the epoxy resin in the modification with **IIb** can be correlated with these relaxations at lower temperatures than the α-relaxation. Such a correlation has been reported in the modification of epoxy resins with reactive rubbers [8, 11].

In general, toughening cured epoxy resins by elastomers should satisfy two requirements: an existence of microphase separated structure and an interfacial bonding between two uncompatibilized phases in the cured resin [12]. The importance of microphase separated structure has been reported for the modification of epoxy resins with a reactive rubber such as CTBN [1]. It has also been reported that pendant epoxy groups of acrylic elastomers, such as BA–VBGE copolymers, are important in the toughening of the network because of the covalent bonding of the epoxy matrix with the epoxy group of the dispersed elastomer particles [7]. The BA–GMA copolymer modification system is thought to satisfy these two requirements. In the system with the BA–GMA copolymers, particle sizes in the range 3.9–6.7 μm would be suitable to improve the toughness of the cured resins. It is interesting that this particle size range is very similar to the most suitable particle size range (4.5–5.9 μm) in the modification with the BA–VBGE–St terpolymers [8].

There is no domain in the modification with the BA–GA elastomer **Ia**. In this modification system, the plastic deformation of the epoxy matrix is more important to reduce the brittleness of the epoxy resin. Such toughening of epoxy resins is observed in the modification with engineering thermoplastics [2–6]. It is interesting that the toughening mechanism varies according to the compatibility of the reactive elastomer used.

In conclusion, modification of the cured epoxy resin with the BA–GA or GMA acrylic copolymers can increase the toughness of the cured resin at minimal expense of mechanical properties. The BA–GA copolymers were more effective as modifiers than the BA–GMA materials. The most suitable compositions for modification of the epoxy resin was inclusion of 20 wt% of the copolymer containing 74 mol% BA and 26 mol% GA units.

Acknowledgement—Authors thank Dr Shinji takeda (Hitachi Chemical Co., Ltd) for the measurements of dynamic mechanical data.

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