TOUGHENING OF EPOXY RESINS BY MODIFICATION WITH REACTIVE ELASTOMERS COMPOSED OF BUTYL ACRYLATE, GLYCIDYL METHACRYLATE AND ACRYLONITRILE OR STYRENE

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Abstract—Acrylic elastomers with pendant epoxy groups were used to improve the toughness of bisphenol-A diglycidyl ether epoxy resin cured with p,p'-diaminodiphenyl sulphone. The elastomers were prepared by terpolymerization of butyl acrylate (BA), glycidyl methacrylate (GMA) and acrylonitrile (AN) or styrene (St). BA–GMA–AN terpolymers were more effective as modifiers for toughening of the epoxy resin system than those containing St. The use of the latter terpolymers tended to separate macroscopically because of poor compatibility with the epoxy matrix. The addition of 20 wt% of the terpolymer (66 mol% BA, 20 mol% GMA and 14 mol% AN units, $\overline{M}_n$ 8700) led to a 40% increase in the fracture toughness (K_{IC}) of the cured resin at slight expense of its mechanical properties. The modified resins had two-phase morphologies in which the volume fraction and average diameter of the dispersed particles were dependent on the structure and concentration of the terpolymers.

The glass transition temperatures of cured resins were equal to or less than that of the parent epoxy resin. The toughening mechanism is discussed in terms of the morphological and dynamic viscoelastic behaviours of the modified epoxy resin system.
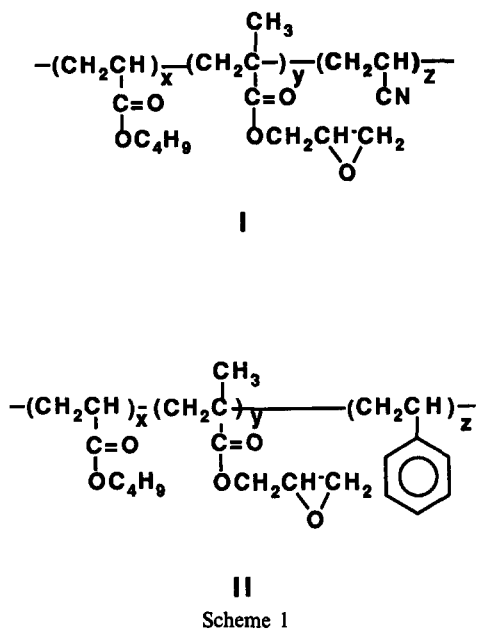
INTRODUCTION

Epoxy resins form the most important thermosetting polymers and have wide use as structural adhesives and matrix resins for fibre composites but their cured resins have one drawback; they are brittle and have poor resistance to crack propagation. The toughness of epoxy resins has been increased by blending with reactive liquid rubbers [1] or terminally functionalized engineering thermoplastics [2–5]. Reactive liquid elastomers with pendant epoxy groups are also effective modifiers, for toughening of the poxy resin system [diglycidyl ether of bisphenol-A (DGEBA) with p,p'-diaminodiphenyl sulphone (DDS)], because of interfacial covalent bonding between the epoxy matrix and dispersed particles as reported previously [6–8]. We have developed such reactive elastomers containing butyl acrylate (BA)–vinylbenzyl glycidyl ether (VBGE) copolymers [6], BA–VBGE–styrene (St) or acrylonitrile (AN) terpolymers [7], and BA–glycidyl (meth)acrylate (GA or GMA) copolymers [8]. In the BA–VBGE copolymer modification system, the dependence of the compatibility of elastomers with epoxy resins on the composition of elastomers has been studied in detail. Elastomers containing more than 86 mol% of BA units had low compatibility with the epoxy matrix. Modification with the elastomer of higher epoxy content (55 mol% BA and 45 mol% VBGE units) resulted in homogeneous structure of cured resins, for which an increase in the fracture toughness could hardly be

observed because of the rigid structure. Elastomer without pendant epoxy groups (70 mol% BA and 30 mol% vinylbenzyl 2-methoxyethyl ether units) was inefficient as a modifier because of the absence of the interfacial adhesion, though the modified resin has a microphase separated structure and its morphology is comparable to that of the resin modified with BA–VBGE elastomer (74 mol% BA and 26 mol% VBGE units), an effective modifier. BA–VBGE–St terpolymers were most effective among the above elastomers as modifiers for the epoxy resin. The addition of 30 wt% of the terpolymer (62 mol% BA, 22 mol% VBGE and 16 mol% St units) led to a 130% increase in the fracture toughness, K_{IC}, of the cured resin at slight expense of mechanical properties. VBGE is an interesting and important compound containing both epoxy and vinyl units but must be prepared via three steps from chloromethylstyrene (a 6:4 mixture of *m*- and *p*-isomers). Then GA or GMA, more convenient epoxides, were used in place of VBGE. The effectiveness for both BA–GA and BA–GMA copolymers as modifiers was comparable to that of BA–VBGE copolymers. It was difficult to obtain copolymers having both the required compatibility with epoxy resins and suitable epoxy contents in these systems. The terpolymerization enabled us to control carefully compatibility and epoxy contents of elastomers as reported previously in the modification of epoxy resins with BA–VBGE–St terpolymers [7].

This paper reports the modification of DDS-cured epoxy resins (diglycidyl ether of bisphenol-A, DGEBA) with acrylic elastomers (I or II), prepared by terpolymerization of BA, GMA and AN or St. The effects of the amount and composition of the

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$$-(CH_2CH)_x-(CH_2\underset{|}{\overset{CH_3}{C}}-)_y-(CH_2CH)_z-$$

with substituents $C=O$, OC_4H_9 (left); $C=O$, $OCH_2CH\cdot CH_2$ / O (middle); CN (right)

I

$$-(CH_2CH)_x-(CH_2\underset{|}{\overset{CH_3}{C}})_y-(CH_2CH)_z-$$

with substituents $C=O$, OC_4H_9 (left); $C=O$, $OCH_2CH\cdot CH_2$ / O (middle); phenyl ring (right)

II

Scheme 1

added elastomers on the toughness of the cured epoxy resin were examined.

EXPERIMENTAL PROCEDURES

Materials

The epoxy resin was the liquid DGEBE [AER 331, Asahi Chemical Industrial Co., Epoxy equivalent weight (EEW) 191]. *p,p'*-Diminodiphenyl sulphone was used as curing agent without further purification. BA, GMA, AN and St were purified in the usual way. Other reagents were used as received.

Measurements

^{1}H-NMR spectra were recorded on a 60 or 90 MHz instrument (JEOL JNM-9MX 60 or 90) using CDCl$_3$ as solvent and tetramethylsilane as internal standard. Molecular weights of terpolymers were determined by gel permeation chromatography (Shimadzu LC-5A instrument) using polystyrene standards. Epoxy groups in polymers were determined by the HCl/dioxane method [9]. Glass transition temperatures of terpolymers and cured resins were measured by differential scanning calorimetry (Shimadzu DSC 41M type). 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-bent geometry at a cross head speed of 1 mm/min (ASTM E-399). 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 speed of 5°/min at frequency of 1 Hz.

Preparation of terpolymers

Terpolymers were prepared as described previously [7, 8]. The composition of BA–GMA–AN terpolymer was obtained from both epoxy and nitrogen contents; that of BA–GMA–St was found by a combination of epoxy content determination and ^{1}H-NMR spectroscopy. The molecular weight of the terpolymer was controlled using dodecanethiol as chain transfer agent.

Curing procedure

A mixture of the epoxy resin and terpolymer was heated at 80° for about 1 hr to homogenize, and the curing agent, DDS, was added to the mixture, which was kept at 120° to dissolve DDS. The resulting mixture was poured into a silicon mould preheated at 100°. The curing cycle was 120°/1 hr + 140°/1 hr + 180°/5 hr. The amount (wt%) of terpolymer used was 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 terpolymer.

RESULTS

Characterization of terpolymers

Table 1 reports some characteristics of acrylic terpolymers, **I** and **II**. The molecular weights of the terpolymers were controlled using dodecanethiol, a chain transfer agent. The terpolymers in Table 1 were designed from the results of the previous paper [6], considering the compatibility of elastomers with the epoxy resin as described in the Introduction.

Mechanical and thermal properties of modified epoxy resins

Figures 1–4 show the mechanical properties of the cured resins as functions of concentration of elastomer, with standard deviations. The cured epoxy resin was transparent but the modified cured resins were opaque.

The flexural strength and modulus for the resin modified with BA–GMA–AN terpolymer **I** decreased with increase in the concentration of terpolymer

Table 1. Preparation and characterization of acrylic terpolymers

No.	Feed composition			C.T.[a] (mol%)	Yield (%)	Terpolymer composition			$\bar{M}_n^b$ 10^{-3}	$\bar{M}_w/\bar{M}_n^b$	EEW[c] (g/eq)	T_g^d (°C)	SP[e]
	BA	GMA	AN(St)			BA	GMA	AN(St)					
Ia	80	15	5	0.67	53	71	22	7	12.8	1.60	568	−35	10.12
Ib	80	15	5	2.0	45	70	22	8	7.6	1.48	560	—	10.14
Ic	75	15	10	2.0	56	66.5	20	13.5	5.8	1.63	600	—	10.25
Id	75	15	10	0.67	61	66	20	14	8.7	1.71	602	−35	10.27
Ie	70	20	10	1.33	69	62	25	13	7.9	1.61	488	−32	10.29
Ig	65	20	15	1.33	54	57.5	24.5	18	7.2	1.66	482	−30	10.42
IIa	80	15	(5)	0.038	58	71	21	(8)	20.3	1.59	623	−34	10.01
IIb	80	15	(5)	0.67	55	72	21	(7)	10.5	1.58	629	−36	10.01
IIc	80	15	(5)	1.33	43	72	21	(7)	7.3	1.55	601	—	10.01
IId	75	17	(8)	3.33	29	66	25	(9)	4.8	1.60	513	—	10.06

[a]Chain transfer agent, dodecanethiol. Based on the total monomer content.
[b]By GPC.
[c]Epoxy equivalent weight (EEW). Determined by HCl/dioxane method.
[d]By DSC.
[e]Calculated by Fedors' method [10]. The SP value $(cal/cm^3)^{1/2}$ for the parent epoxy resin is 10.60.

(Fig. 1). The use of **Ia** (71 mol% Ba, 22 mol% GMA and 7 mol% AN units, $\bar{M}_n$ 12,800) tended to separate macroscopically as shown later in the morphology of the modified resin. Terpolymer **Ib** (70 mol% BA, 22 mol% GMA and 8 mol% AN units, $\bar{M}_n$ 7600) had lower compatibility with the epoxy resin than the higher molecular weight material **Ia** of similar composition. On addition of 15 wt% of **Ib**, the modified resin could not be obtained owing to separation of sticky material containing a large amount of **Ib** in the surface of the cured resin. In the modification with **Ic** (66.5 mol% BA, 20 mol% GMA and 13.5 mol% AN units, $\bar{M}_n$ 5800), the flexural strength for the cured resin decreased linearly with increasing **Ic** content. 10 wt% addition of **Id** (66 mol% BA, 20 mol% GMA and 14 mol% AN units, $\bar{M}_n$ 8700) led to an abrupt decrease in flexural strength. The extent of decrease in flexural properties was less for modification with both **Ie** (62 mol% BA, 25 mol% GMA and 13 mol% AN units, $\bar{M}_n$ 7900) and **Ig** (57.5 mol% BA, 24.5 mol% GMA and 18 mol% AN units, $\bar{M}_n$ 7200) than in the other modification systems.

The fracture toughness (K_{IC}) of the modified resin depended on the composition and molecular weight of terpolymer I (Fig. 2). Terpolymer **Ia** was less effective than the others. The K_{IC} values for the Ic-modified resins increased linearly with increase in Ic content but the use of more than 20 wt% led to macrophase separation. The dependence of K_{IC} value for resins modified with **Id** on the terpolymer content was specific and interesting but, on addition of 25 wt% of **Id**, the cured resin could not be obtained because of separation of a small amount of sticky material containing **Id**. In the modification with **Ie**, the K_{IC} value for the cured resin increased with increasing terpolymer content up to 25% at slight expense of its mechanical properties. Fractural behaviour in the modification with **Ig** was similar to that with **Ie** but the increase in K_{IC} value for the former was somewhat smaller than for the latter.

Flexural properties of the resins modified with BA–GMA–St terpolymers **II** also decreased with
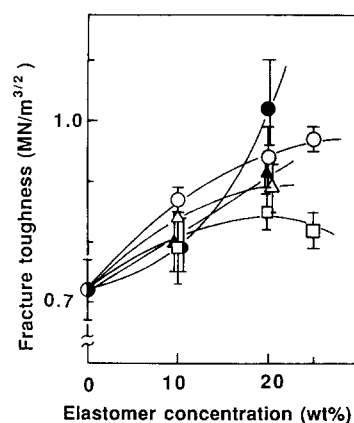
Fig. 2. Dependence of fracture toughness (K_{IC}) for modified resins on terpolymer I concentration and structure. ◑, Control; □, **Ia**; ▲, **Ic**; ●, **Id**; ○, **Ie**; △, **Ig**.

increase in the terpolymer concentration as well as those with AN-containing terpolymers I (Fig. 3). Increase in K_{IC} value, on addition of **II**, was smaller than in the modification with I (Fig. 4). In the modification with **IIa** (71 mol% BA, 21 mol% GMA and 8 mol% St units, $\bar{M}_n$ 20,300), K_{IC} for the cured resin increased 10% on addition of 10 wt% of **IIa** but decreased with 20 wt%. K_{IC} of the resins modified with **IIb** (71 mol% BA, 21 mol% GMA and 7 mol% St units, $\bar{M}_n$ 10,500) increased linearly with increase in **IIb** content. The use of both **IIc** (72 mol% BA, 21 mol% GMA and 7 mol% St units, $\bar{M}_n$ 7300) and **IId** (66 mol% BA, 25 mol% GMA and 9 mol% St units, $\bar{M}_n$ 4800) led to cured resins with macrophase-separated structure. Among the elastomers of similar composition (**IIa**, **IIb** and **IIc**) **IIc** with the lowest molecular weight had the poorest compatibility with the epoxy resin.

Figure 5 shows the glass transition temperatures, T_g, of the cured resins. T_gs for the resins modified with either I or II were equal to or less than T_g for the parent epoxy resin.

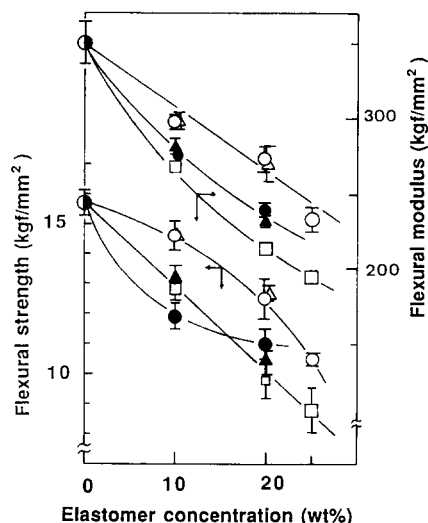Fig. 1. Flexural strength and modulus of terpolymer I-modified resins as function of terpolymer concentration and structure. ◑, Control; □, **Ia**; ▲, **Ic**; ●, **Id**; ○, **Ie**; △, **Ig**.
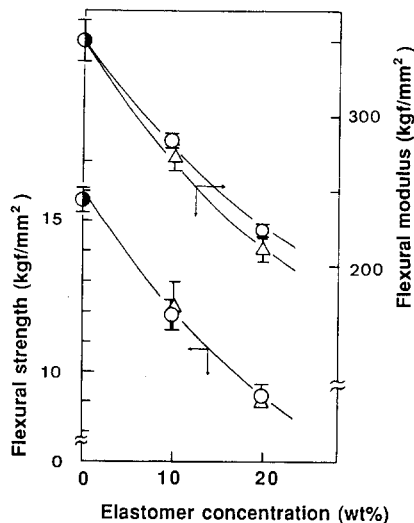
Fig. 3. Flexural strength and modulus of terpolymer II-modified resins as function of **II** concentration and structure. ◑, Control; △, **IIa**; ○, **IIb**.
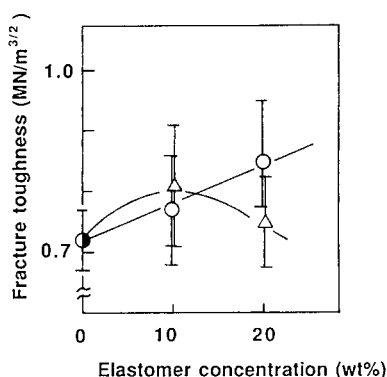
Fig. 4. Dependence of fracture toughness (K_{IC}) for modified resins on copolymer II concentration and structure. ◑, Control; △, IIa; ○, IIb.

Morphology of the modified resins

Figures 6 and 7 show scanning electron micrographs (SEMs) of the modified resins. Morphological data for the cured resins modified with either I or II are collected in Table 2. The unmodified resin had only one phase, and the fracture surface was smooth and featureless as reported previously [6] but, for the elastomer-modified resin, two-phase morphology was seen with the epoxy-rich phase being the continuous matrix and the elastomer-rich phase forming dispersed spherical particles. The volume fraction (V_f), the average diameter (D), and the number (N) of the particles were dependent on the composition and content of the terpolymer used. The volume fraction of dispersed particles for modification with Ia containing 71 mol% of BA increased with increasing Ia content and was larger than the weight fraction of the terpolymer added in the cured system. The particle size hardly changed with increasing terpolymer Ia concentration up to 25 wt%. Morphologies of the resins modified with terpolymer Ia indicate the tendency to separate macroscopically [Fig. 6(A)]. On addition of 10 wt% of Ib, the size and volume fraction of particles were less than for the modified resin with 10 wt% of Ia. The particles for the resin modified with Ic of the lower BA content (66.5 mol%) were smaller than for the modification with Ia of the higher BA content (71 mol%) (Table 2). Morphologies of the modified resins with moderate molecular weight Id ($\bar{M}_n$ 8700) were similar to
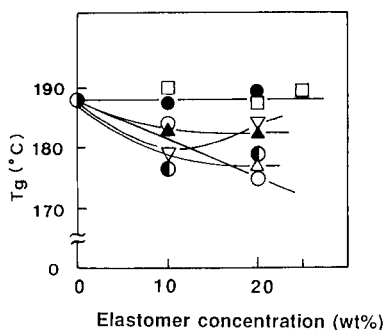

Fig. 5. Glass transition temperature (T_g) of the cured resin. ◑, Control; □, Ia; ▲, Ic; ●, Id; ◐, Ie; △, Ig; ▽, IIa; ○, IIb.
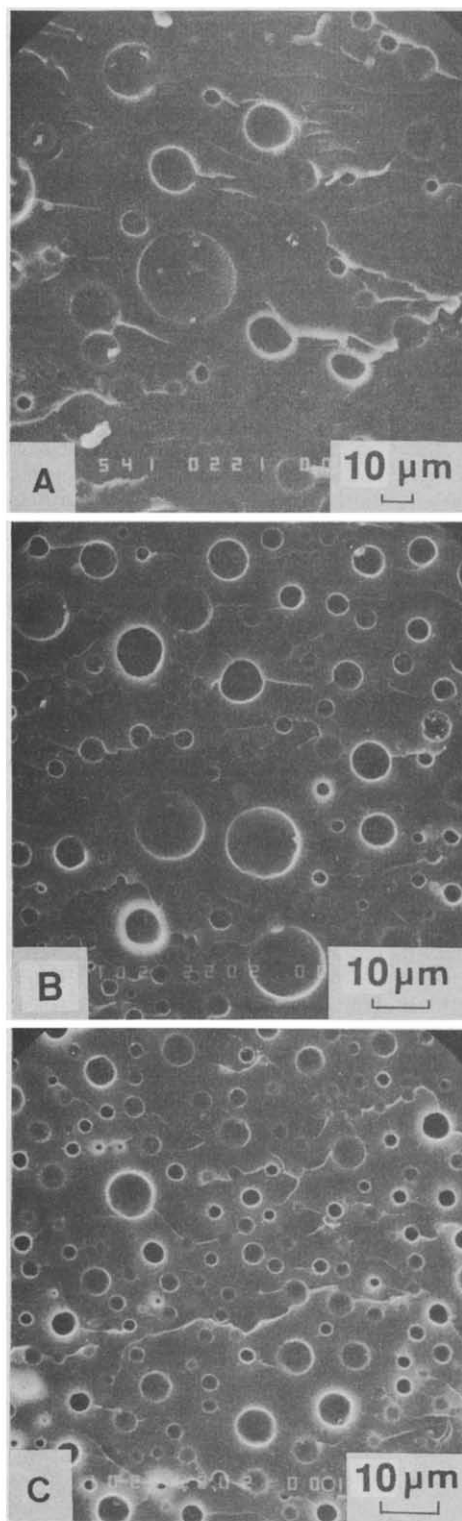

Fig. 6. SEMs of fracture surfaces for the modified resins with 20 wt% of BA–GMA–AN terpolymers I. (A) Ia; (B) Id; (C) Ie.

those with lower molecular weight Ic ($\bar{M}_n$ 5800) of similar composition [Fig. 6(B)]. The particle sizes in the modifications with Ie or Ig containing fewer BA units were similar to that with Ic containing more BA units, but the particle size distribution in the former
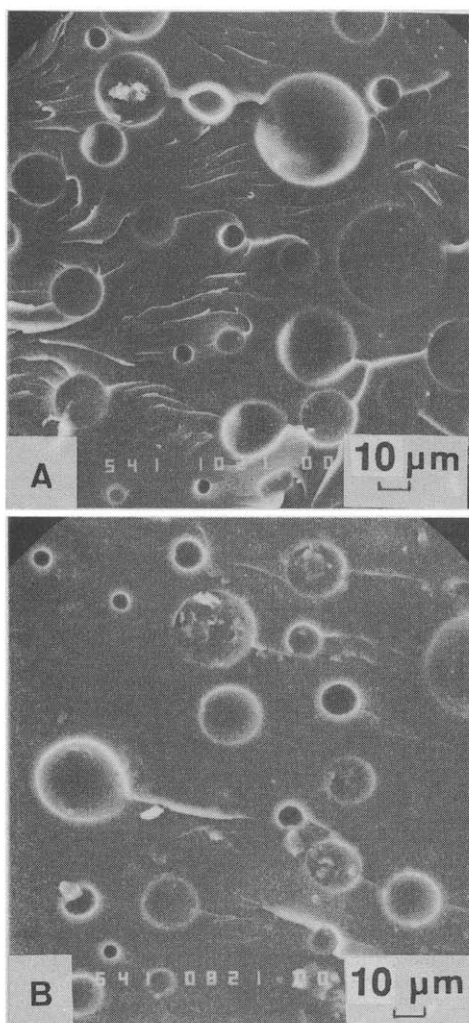
Fig. 7. SEMs of fracture surfaces for the modified resins with 20 wt% of BA–GMA–St terpolymers II. (A) IIa; (B) IIb.

was far smaller than that in the latter [Fig. 6(C) and Table 2].

The sizes of the dispersed particles for the cured resins in the modification with BA–GMA–St terpolymers II were greater than for the modification with BA–GMA–AN I. The particle size distribution in the former system was also larger than that in the latter. The sizes and volume fraction of the particles for the modification with higher molecular weight IIa ($\bar{M}_n$ 20,300) were larger than those with lower molecular weight IIb ($\bar{M}_n$ 10,500) of similar composition [Figs 7(A) and (B)].

Dynamic viscoelastic analysis of the modified resins

Dynamic viscoelastic analysis can give information on micro-structures of cured resins. Figure 8 shows the storage moduli, G', and tan δ curves for the resins modified with Id. The peak position of the α-relaxation in the tan δ curves hardly changed but it became broader with increase in Id content, compared with dynamic viscoelastic behaviour for the parent epoxy resin. The magnitude of several relaxations at ca $50°$–$180°$ became larger, and a new relaxation ap-

peared at ca $-20°$, and increased with increasing Id content. The storage modulus decreased with increasing Id content.

In the modification with Ie, the peak position of the α-relaxation in the tan δ curves shifted slightly towards lower temperature, its magnitude decreased, and it became broader with increase in elastomer content (Fig. 9). The magnitude of the new relaxation at ca $-20°$ in the modified resin with Ie was smaller than in the Id modified system. This result indicates that the tendency to phase-separate is smaller for the former system than for the latter. Dynamic viscoelastic behaviour at temperatures lower than the α-relaxation for the Ie-modified resins were similar to those for the Id-modified systems.

DISCUSSION

Reactive elastomers I with pendant epoxy groups were effective modifiers for improving the toughness of the epoxy resin system. Terpolymers II were less effective because of poor compatibility with the epoxy resin. The control of terpolymer composition is important to obtain more effective modifiers in systems with reactive elastomers containing BA units. The composition dependence of compatibility with the epoxy resin might be explained by the solubility parameter (SP) of the elastomers (see Table 1).

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

In modification with BA–GMA–AN terpolymers I, materials Id and Ie are comparable, considering the extent of both the decrease in flexural properties and the increase in fracture toughness; the K_{IC} value for the Id-modified resin is slightly larger than that for the Ie-modified when using 20 wt%, but the flexural strength for the former is smaller than that for the latter. The resins modified with terpolymers I have two-phase morphologies (Fig. 6). The morphologies of the fracture surface for resins modified with Id or Ie show that the average particle sizes hardly changed with increasing elastomer content and that the volume fractions of particles were larger than the weight fraction of the elastomer used (Table 2). These results indicate that the epoxy resin was incorporated into the dispersed particles to some extent but that the extent of incorporation is somewhat different in the two types of systems. The volume fraction of particles for the Id-modified resins is larger than that for the Ie-modified. These morphological characteristics correspond to the results by dynamic viscoelastic analysis. The dynamic mechanical results show that the α-relaxation peak position in the tanδ curves hardly changed with increasing Id content, but slightly shifted in the Ie-modification, and that the appearance of the new relaxation at ca $-20°$ was more significant in the Id-modified resins than in the Ie-modified. The emergence of the new relaxation in the region of T_g of the elastomer indicates the occurrence of phase-separation. The T_gs ($-30°$ $-36°$) for the elastomers used in this study are shown in Table 1. In general, T_g obtained by dynamic viscoelastic analysis is higher than that by DSC. Increase in K_{IC} for the modified resin can be correlated with the lower temperature relaxation height (or area) [7, 12].
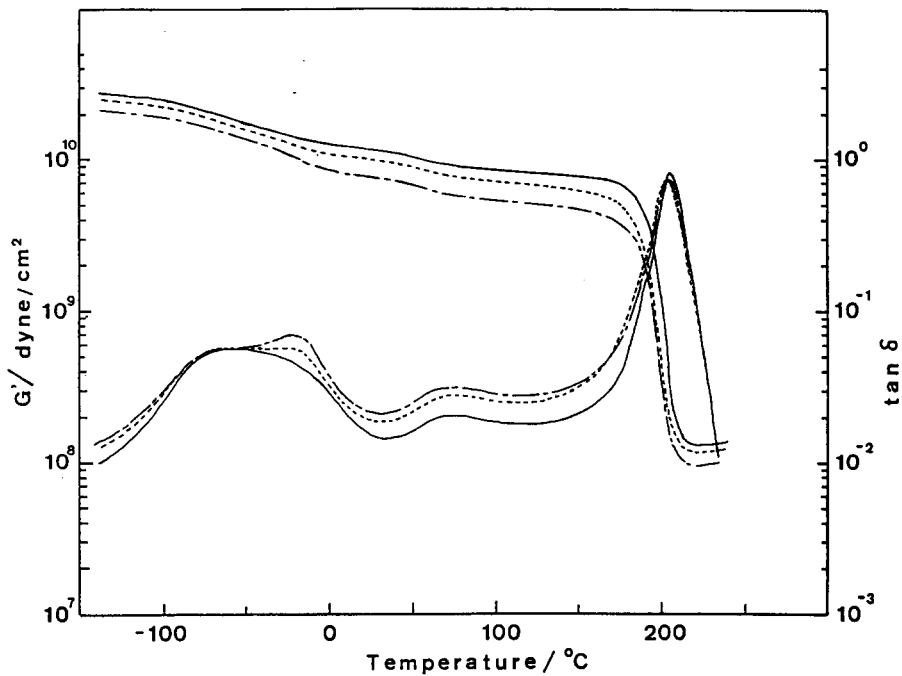
Fig. 8. Dynamic viscoelastic analysis for Id-modified resin. ——, Control; ----, Id 10 wt% addition; —·—, Id 20 wt% addition.

Increase in the magnitude of several relaxations at *ca* 50–180° is found for modification with Id or Ie. The increase in the magnitude of the tan δ curves is due to intermixing of the epoxy resin and the elastomer in various compositions. The toughening of the epoxy resin in the modification with BA–GMA–AN elastomers can be also correlated with these relaxations at temperatures below the α-relaxation as reported previously [8].

Morphological behaviour of resins modified with Id or Ie is interesting in connection with the relation between mechanical properties and morphologies of the modified epoxy resins. The tendency to decrease flexural properties with increasing elastomer content is larger in the Id-modified resin than in the Ie-modified (Fig. 1). The particle sizes of the resin modified with Ie are similar to those with Id but the extent of the dispersion of particle sizes in the former
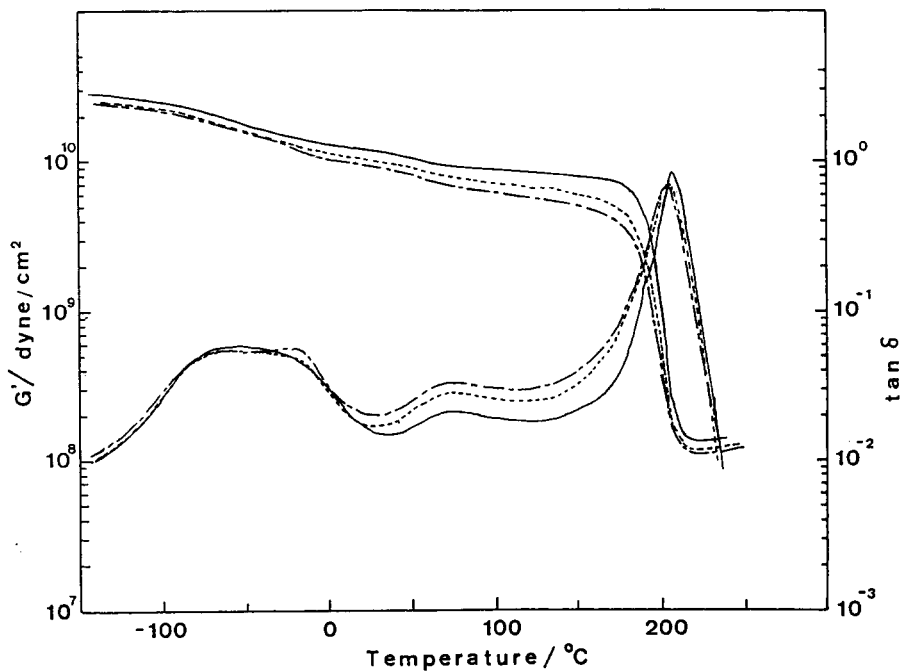

Fig. 9. Dynamic viscoelastic analysis for Ie-modified resin. ——, Control; ----, Ie 10 wt% addition; —·—, Ie 20 wt% addition.

Table 2. Morphological results

Resin composition DGEBA/terpolymer	Feed terpolymer[a] weight fraction	D^b	V_f^c	N^d
100/0	0	—	0	0
Ia series				
90/10	0.077	8.7 ± 3.4	0.122	0.4
80/20	0.157	11.5 ± 6.2	0.227	0.2
75/25	0.197	8.0 ± 3.0	0.261	0.5
Ib series				
90/10	0.077	4.0 ± 3.1	0.098	0.5
85/15	0.117	—[e]	—[e]	—[e]
Ic series				
90/10	0.077	3.8 ± 2.9	0.130	0.6
80/20	0.156	3.2 ± 1.5	0.265	2.9
Id series				
90/10	0.077	2.7 ± 2.6	0.123	1.4
80/20	0.156	3.4 ± 2.3	0.195	1.5
Ie series				
90/10	0.077	2.8 ± 1.1	0.105	1.5
80/20	0.156	2.5 ± 1.2	0.142	2.5
75/25	0.196	2.5 ± 0.5	0.252	5.2
Ig series				
90/10	0.077	3.0 ± 0.6	0.127	1.8
80/20	0.156	2.7 ± 0.7	0.216	2.9
IIa series				
90/10	0.077	14.2 ± 8.1	0.161	0.1
80/20	0.156	16.4 ± 8.4	0.280	0.1
IIb series				
90/10	0.077	8.2 ± 3.7	0.105	0.2
80/20	0.156	15.2 ± 6.6	0.194	0.1

[a]Based on the total resin.
[b]Average particle diameter in μm. The $\pm x$ 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.

case is far smaller than in the latter. A decrease in the dispersion of particle sizes might affect the decrease in mechanical properties of modified resins (Table 2). These results give important information about the molecular design of effective elastomers as modifiers.

The effectiveness of BA–GMA–AN terpolymers was, unexpectedly, comparable to that of BA–GMA copolymers in spite of the molecular design based on the results of the previous paper [6–8]. In the modification system with elastomers containing VBGE as an epoxide unit, both BA–VBGE–St and BA–VBGE–AN terpolymers are far more effective as modifiers than BA–VBGE copolymers. The addition of 30 wt% of the terpolymer (62 mol% BA, 22 mol% VBGE and 16 mol% St units) led to a 130% increase in K_{IC} with slight deterioration of mechanical properties, and K_{IC} of resin modified with 30 wt% of the AN-containing terpolymer (62 mol% BA, 25 mol% VBGE and 13 mol% AN units) resulted in a 95% increase [7]. On addition of 20 wt% of the copolymer (74 mol% BA and 26 mol% VBGE units), K_{IC} of the modified resin increased only 30% and slightly decreased with the use of 30 wt% [6]. In the modification with BA–GMA copolymers, the use of 30 wt% of the copolymer (73 mol% BA unit) caused a 50% increase in K_{IC} [8]. It is thought that the extent of increase in the fractural toughness in the modification with BA–GMA–AN terpolymer would be particularly low, compared with these results. The present results could be explained by both the morphology of the modified resins and elasticity of the dispersed particles.

Morphological behaviour of the modified resins is interesting and suggests a relationship between the effectiveness of the modifier and its structure or composition. In the modification with epoxy-containing acrylic elastomers, the most suitable range of particle sizes is 2.2–2.8 μm for BA–VBGE copolymers [6], 4.5–5.9 μm for BA–VBGE–St terpolymers [7], 1.3–4.4 μm for BA–VBGE–AN, and 3.9–6.7 μm for BA–GMA copolymers [8]. In the modification with the present elastomers **I**, the suitable range of the particle sizes is 2.5–3.4 μm. It is noteworthy that this size range of the particle is similar to that in the modification with BA–VBGE copolymers which are less effective modifiers. The size range of the particle for the resins modified with BA–GMA–AN terpolymers is thought to be somewhat smaller than the most suitable size for the reactive butyl acrylate elastomers. In modification with amine-terminated butadiene–acrylonitrile rubbers (ATBN), the suitable particle sizes (4–5 μm) [13] are similar to those in the more effective modifier, BA–VBGE–St terpolymers, among the present reactive acrylic elastomers. It is interesting that there are most suitable particle sizes, independent of the structure and composition of elastomers, in the modification with reactive rubbers. The unexpected results in the modification with terpolymers **I** could be explained partly by the morphologies of the modified resins.

It is interesting and instructive to consider how the particles would disperse in the epoxy matrix and if the dispersed particles would maintain their elasticity. In the previous papers, BA–VBGE copolymer of higher epoxy content (VBGE 45 mol%) was ineffective because of the homogeneous structure of the modified resin, but BA–GA copolymer was effective in spite of the absence of two-phase morphology in the modified resin. These results could be explained by the elasticity of the copolymers used and ductility of the

resulting matrix [8]. Furthermore, a comparison of BA–GMA–AN terpolymers with BA–GMA copolymers as modifiers is instructive: the volume fraction of dispersed particles is larger than the weight fraction of the elastomers used in the modification with the former, but equal to or smaller than that in the modification with the latter. This difference indicates that a greater amount of the epoxy resin would be incorporated into the particles in the former resins than in the latter. Elasticity of dispersed particles would be partially lost by incorporation of the epoxy resin in the modification with BA–GMA–AN terpolymers but its extent would be less in the BA–GMA modification system. The dispersed particles act as stress concentrators in the fracture of the modified resin, induce delocalized plastic deformation of the matrix around the particles, and dissipate the fracture energy. In such a toughening mechanism, not only elasticity of the elastomer but also the maintenance of elasticity of the resulting particles would be necessary to improve the toughness of the epoxy resin after modification with reactive elastomer. The unexpected results in the modification with BA–GMA–AN terpolymers would be also explained partly by decrease in elasticity of the dispersed particles in the matrix.

In conclusion, modification of the cured epoxy resin with BA–GMA–AN terpolymers can increase the toughness of the cured resin at minimal expense of mechanical properties. The suitable compositions for modification of the epoxy resin were inclusion of 20 wt% of terpolymer Id (66 mol% BA, 20 mol% GMA and 14 mol% AN units, $\bar{M}_n$ 8700) or Ie (62 mol% BA, 25 mol% GMA and 13 mol% AN units, $\bar{M}_n$ 7900). BA–GMA–St terpolymers are less

effective because of their poor compatibility with the epoxy resin compared with BA–GMA–AN.

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