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TOUGHENING OF EPOXY RESINS BY MODIFICATION WITH ACRYLIC ELASTOMERS CONTAINING PENDANT EPOXY GROUPS

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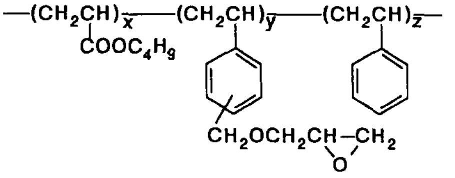
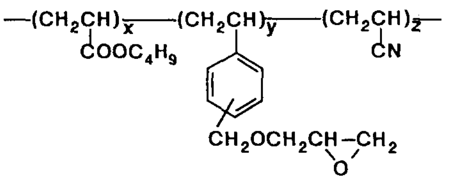
Abstract—New acrylic elastomers with pendant epoxy groups were used to reduce the brittleness of bisphenol-A diglycidyl ether epoxy resin cured with *p,p*′-diaminodiphenyl sulphone. The elastomers were prepared by copolymerization of butyl acrylate (BA), vinylbenzyl glycidyl ether (VBGE) and styrene (St) or acrylonitrile (AN). These terpolymers were effective for toughening of the epoxy resin system. The addition of 20 wt% of the terpolymer (74 mol% BA, 18 mol% VBGE and 8 mol% St) resulted in an 80% increase in the fracture toughness (K_{Ic}) of the cured resin at the slight expense of its mechanical properties. The modified epoxy resins had two-phase morphology in which the volume fraction and average diameter of the dispersed elastomer particles were dependent on the structure and concentration of the terpolymer. The toughening mechanism is discussed in terms of the morphological and dynamic mechanical behaviour of the modified epoxy resin system.

INTRODUCTION

The toughness of epoxy resins has been increased by blending with reactive liquid rubbers [1] or terminally functionalized engineering thermoplastics [2]. In a previous paper [3] epoxide-containing acrylic rubbers, prepared by copolymerization of *n*-butyl acrylate (BA) with vinylbenzyl glycidyl ether (VBGE), have been reported as decreasing the brittleness of epoxy resins. It has also been reported that the microphase separation of cured resin and its interfacial binding are necessary to improve the brittleness of epoxy resin by modification with elastomers [3]. In this copolymer system, the compatibility of elastomers with epoxy resins depended on the composition of elastomers and the interfacial binding was achieved by the covalent bonding of epoxy resins with pendant epoxy groups of elastomers. Elastomers containing more than 86 mol% of BA units had low compatibility with epoxy matrix. The elastomer without pendant epoxy group (70 mol% BA and 30 mol% vinylbenzyl 2-methoxyethyl ether) was an inefficient modifier, though the cured resin has a two-phase morphology comparable to that modified with BA-VBGE elastomer (74 mol% BA and 26 mol% VBGE), an effective modifier. Modification with the elastomer of higher epoxy content (45 mol% VBGE) resulted in homogeneous structure of cured resin, where an increase in the fracture toughness of cured resins was hardly observed owing to the rigid structure. It was difficult to obtain copolymers having both relevant compatibility with epoxy resins and suitable epoxy contents. The terpolymerization will enable us to control carefully compatibility and epoxy contents of elastomers.

This paper reports the modification of *p,p*′-diaminodiphenyl sulphone (DDS)-cured epoxy resins (diglycidyl ether of bisphenol A, DGEBA) with new acrylic elastomers(I and II) containing pendant epoxy groups, prepared by copolymerization of BA, VBGE and styrene (St) or acrylonitrile (AN),


(I)


(II)

The effect of the amount and composition of added terpolymer on the toughness of the cured epoxy resin was examined.

EXPERIMENTAL PROCEDURES

Materials

The epoxy resin was the liquid bisphenol A-type epoxy resin [Epikote 828, Shell Chemical Co., epoxy equivalent weight (EEW) 190]. *p,p*′-Diaminodiphenyl sulphone (Tokyo Chemical Ind. Co.) was used as a curing agent without further purification. Vinylbenzyl glycidyl ether (VBGE) was prepared by the phase transfer catalysed reaction of vinylbenzyl alcohol and epichlorohydrin as previously [3]. 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 FX 900) 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 [4]. Acrylonitrile contents of polymers were determined by elemental analysis for nitrogen. Glass transition temperatures of cured resins were determined 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 K7113) were obtained at a cross head speed of 2 mm/min. Fracture toughness (K_{1c}, 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. Dynamic mechanical analysis was performed with a DuPont DMA 982 instrument between −130° to 220° at a heating rate of 5°/min at variable frequency of 30–2 Hz.

Preparation of terpolymers

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. Terpolymers were isolated using hexane as precipitant and purified twice by reprecipitation with tetrahydrofuran/hexane. The liquid terpolymers were dried overnight *in vacuo* at 60°. The composition of BA/VBGE/St terpolymer was found by a combination of epoxy content determination and ^{1}H-NMR spectroscopy; that of BA/VBGE/AN was obtained from both epoxy and nitrogen contents.

Curing procedure

A mixture of the epoxy resin and terpolymer 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 140° 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 180° for 5 hr. The amount (wt%) of terpolymer used was calculated, based on the amount of Epikote 828. The curing agent was used stoichiometrically to the total epoxy content of both the epoxy resin and terpolymer.

RESULTS

Characterization of terpolymers

Table 1 reports some characteristic properties of acrylic elastomers **I** and **II**. The terpolymer with desired composition can be easily prepared by this method. The terpolymers in Table 1 were designed on the basis of results of the previous paper [3], where the addition of the acrylic copolymer with 55% of BA and 45% of VBGE units could not increase the fracture toughness of the cured resin because of its good compatibility with the parent epoxy resin.

Mechanical and thermal properties of modified epoxy resins

Figures 1–6 show the effect of addition of the elastomers on the mechanical properties of the cured resins. The cured parent epoxy resin was transparent but the elastomer-modified cured resins were opaque or translucent.

The tensile strength and modulus for the cured resin modified with St-containing elastomers **I** decreased with increase in the elastomer concentration (Fig. 1). The dependences of the flexural strength and modulus for the modified epoxy resins on the concentration and composition of the added terpolymer were similar to that of the mechanical properties obtained by the tensile test (Fig. 2). The toughness of the epoxy resin modified with **I** depended on the composition and molecular weight of **I**. In the modification of the epoxy resin with **Ia** containing 62 mol% of BA unit (Table 1), increase in the fracture toughness (K_{1c}) of the cured resin was nearly proportional to the increase in the elastomer content as shown in Fig. 3. In the modification with another elastomer containing a larger proportion of BA units (74 mol%), the K_{1c} value increased with increasing terpolymer content up to 20 wt% and then decreased (Fig. 2). The use of the higher molecular weight

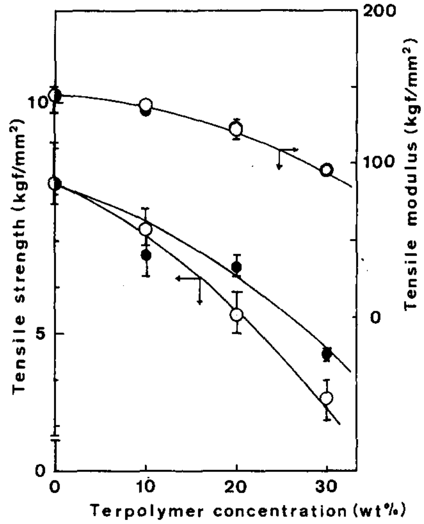


Fig. 1. Tensile strength and modulus of terpolymer-modified epoxy resins as function of terpolymer concentration and structure. (●) BA/VBGE/St 62/22/16 (**Ia**); (○) BA/VBGE/St 74/18/8 (**Ib**).

Table 1. Preparation and properties of acrylic terpolymers

	Feed composition (mol%)				Copolymer composition* (mol%)							
No.	BA	VBGE	St(AN)	Yield (%)	BA	VBGE	St(AN)	M_n† 10^{-3}	M_w† 10^{-3}	M_w/M_n	EEW‡	SP§ $(cal/cm^3)^{1/2}$
Ia	70	20	10	66	62	22	16	10.5	16.8	1.60	632	10.14
Ib	80	15	5	56	74	18	8	8.2	14.2	1.73	751	10.04
Ic	80	15	5	62	73	17	10	22.3	42.5	1.91	788	10.05
IIa	70	20	(10)	61	62	25	(13)	16.8	30.0	1.78	523	10.35
IIb	65	20	(15)	64	56	25	(19)	13.4	24.7	1.84	523	10.49

*Calculated from both epoxy equivalent and ^{1}H-NMR spectroscopy in St-containing terpolymers and from both epoxy equivalent weight and elemental analysis for nitrogen in AN-containing terpolymers.

†Measured by GPC.

‡Epoxy equivalent weight determined by HCl/dioxane method.

§Calculated by Fedors' method [5]. The SP value for the parent epoxy resin is 10.60.

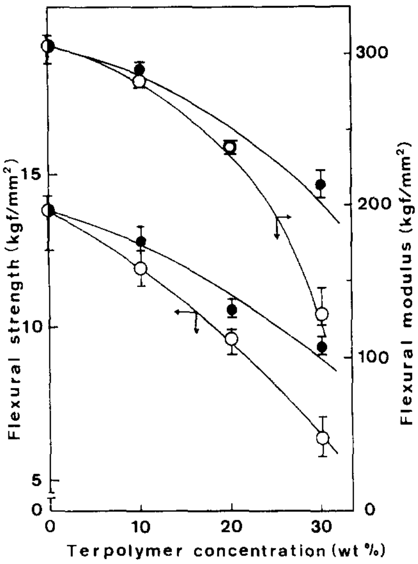


Fig. 2. Flexural strength and modulus of terpolymer-modified epoxy resins as function of terpolymer concentration and structure. (●) BA/VBGE/St 62/22/16 (**Ia**); (○) BA/VBGE/St 74/18/8 (**Ib**).

elastomer in the modification resulted in a decrease in K_{1c}, though the mechanical properties of the modified cured resin hardly changed. For example, the K_{1c} values after modification with elastomer **Ic** ($\bar{M}_n$ 22,300) were smaller than those with the lower molecular weight material (**Ib**, $\bar{M}_n$ 8200) in spite of the similar compositions of the elastomers as shown in Fig. 3.

The tensile and flexural properties of the epoxy resin modified with AN-containing elastomers **II** decreased with increase in the elastomer concentration to a smaller extent than those modified with St-containing elastomer **I** (Figs 4 and 5). An increase in the K_{1c} value, on addition of **II**, was also smaller than that in the modification with **I**. The K_{1c} of the cured resin, modified with the elastomer containing 13 mol% of AN units, increased linearly with increase in the elastomer content. In the toughness tests of the cured resin, modified with elastomer containing 19 mol% of AN units, K_{1c} increased with increasing elastomer content up to 20 wt% and then decreased slightly.

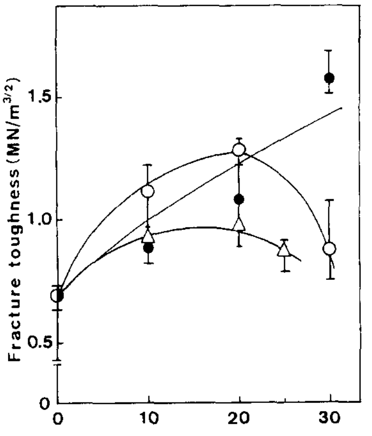


Fig. 3. Dependence of fracture toughness (K_{1c}) for terpolymer-modified epoxy resin on terpolymer concentration and structure. (●) BA/VBGE/St 62/22/16 (**Ia**); (○) BA/VBGE/St 74/18/8 (**Ib**); (△) BA/VBGE/St 73/17/10 (**Ic**).

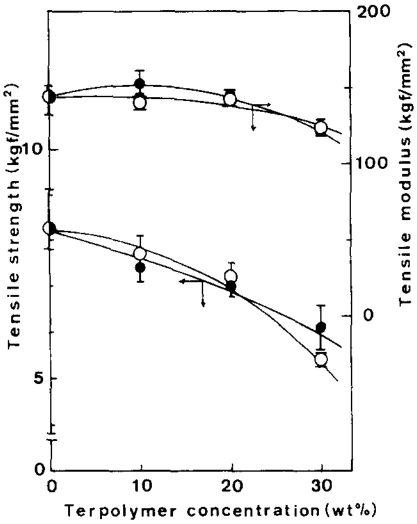


Fig. 4. Tensile strength and modulus of terpolymer-modified epoxy resins as function of terpolymer concentration and structure. (○) BA/VBGE/AN 62/25/13 (**IIa**); (●) BA/VBGE/AN 56/25/19 (**IIb**).

Figure 7 shows the glass transition temperatures, T_g, of the cured resins. The T_g values for resins modified with **I** were similar to and those for resins modified with **II** nearly equal to or less than T_g for the parent epoxy resin. The T_gs of the former resins are similar to those for modification with elastomers containing BA and VBGE units reported previously [3].

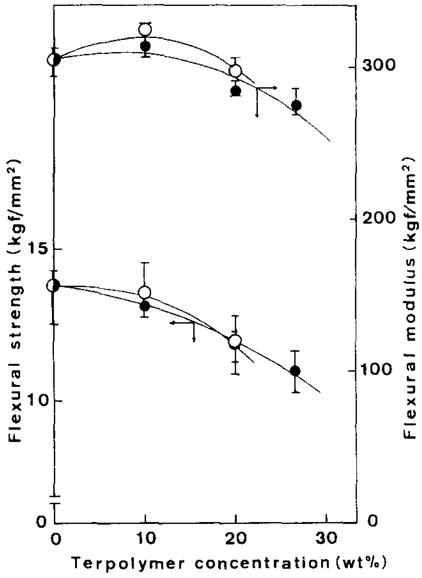


Fig. 5. Flexural strength and modulus of terpolymer-modified epoxy resins as function of terpolymer concentration and structure. (○) BA/VBGE/AN 62/25/13 (**IIa**); (●) BA/VBGE/AN 56/25/19 (**IIb**).

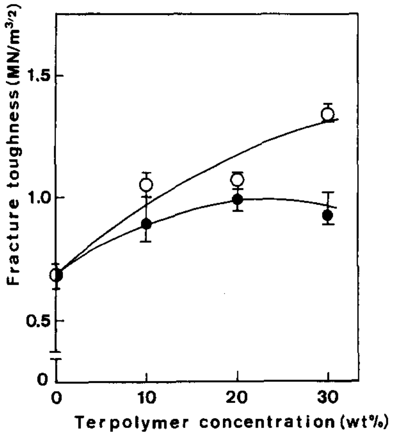


Fig. 6. Dependence of fracture toughness (K_{Ic}) for terpolymer-modified epoxy resin on terpolymer concentration and structure. (○) BA/VBGE/AN 62/25/13 (**IIa**); (●) BA/VBGE/AN 56/25/19 (**IIb**).

Morphology of the cured resins

Figure 8 shows the scanning electron micrographs (SEMs) of the cured resins. The morphology of the fracture surface for the elastomer-modified epoxy resins was quite different from that for the parent epoxy resin. The unmodified epoxy resin has only one phase but, for the elastomer-modified resin, a two-phase morphology was seen with the epoxy-rich phase forming the continuous matrix and the terpolymer-rich phase forming dispersed spherical particles. Table 2 shows the volume fraction, V_p, and diameter, D, of the dispersed particles as obtained from SEMs. The volume fraction, size and number of the particles were strongly dependent on the composition and concentration of the terpolymer. The volume fraction of the dispersed particles for the modification with **Ib** containing 74 mol% of BA increased with increasing elastomer concentration but its volume fraction was nearly equal to the weight fraction of the terpolymer added in the cured system. The particle size did not change when the elastomer concentration increased up to 20 wt% but the size almost doubled on addition of 30 wt% of the elastomer. The volume fraction and size of the dispersed particles for the cured resin modified with **Ia** containing 62 mol% of BA were smaller than those for modification with **Ib** of the higher BA content (74 mol%). The size of the dispersed particle for modification with **Ic** ($\bar{M}_N$ 22,300) was larger than that with **Ib** ($\bar{M}_n$ 8000) in spite of the similar compositions of the terpolymers. The V_p values of the dispersed particle for the former system could not be obtained as its particle number was smaller than others (Table 2).

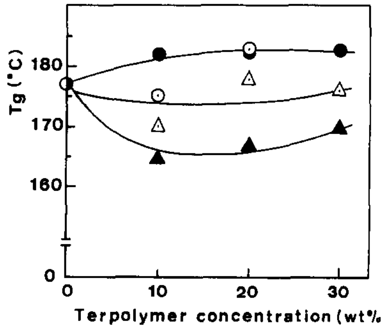


Fig. 7. Glass transition temperature (T_g) of the cured resin. (●) **Ia**; (○) **Ib**; (△) **IIa**; (▲) **IIb**.

The volume fraction of the dispersed particle for modification with AN-containing terpolymer **II** was much smaller than that for modification with St-containing terpolymer **I**. Further, the small dependence of the volume fraction and size of the dispersed particle on the composition and concentration of **II** was also observed, compared to the dependence in the system containing terpolymer **I** (see Table 2).

Dynamic mechanical analysis of the cured resins

Dynamic mechanical analysis (DMA) can give information on the micro-structure of cured resins. Figures 10–13 show DMA results for the resins modified with **I** and **II**, respectively.

The tan δ curve for the resins, modified with 10–20 wt% of **Ib** (74 mol% BA and 8 mol% St) did not change except for an increase in low temperature relaxation around 0°, compared to that for the parent epoxy resin. The 10 wt% addition system is omitted' from Fig. 10. There is a small decrease in storage modulus over the range of the temperature considered in the modification with 10–20 wt% of the elastomer compared to the unmodified epoxy resin (Fig. 11). The tan δ curve for the cured resin on the addition of 30 wt% of **Ib** altered considerably: the peak position of the α-relaxation shifted from 210 to 180° and its magnitude decreased. The low temperature relaxation around −45° also decreased and the magnitude of the new low temperature relaxation around 0° persisted. The storage modulus decreased considerably around 140°.

Table 2. Morphological data

Resin composition Epoxy/terpolymer	Feed terpolymer* weight fraction	D†	V_f‡	N§
100/0	0	—	0.000	0
Ia series				
90/10	0.078	2.4	0.006	0.1
80/20	0.158	2.9	0.117	1.6
70/30	0.242	5.9	0.237	0.8
Ib series				
90/10	0.078	5.0	0.054	0.6
80/20	0.159	4.5	0.172	1.0
70/30	0.240	10.2	0.239	0.2
Ic series				
90/10	0.077	14.6	—¶	0.06
80/20	0.160	18.0	—¶	0.04
70/30	0.226	19.0	—¶	0.06
IIa series				
90/10	0.077	4.4	0.037	0.2
80/20	0.157	3.8	0.098	0.7
70/30	0.230	1.3	0.054	3.8
IIb series				
90/10	0.077	2.6	0.026	0.6
80/20	0.157	2.8	0.083	1.0
70/30	0.230	4.3	0.081	0.5

*Based on the total resin.
†Average particle diameter in μm.
‡Volume fraction of dispersed particle.
§Number of particle/100 μm^2.
¶Not obtained owing to smaller particle number.

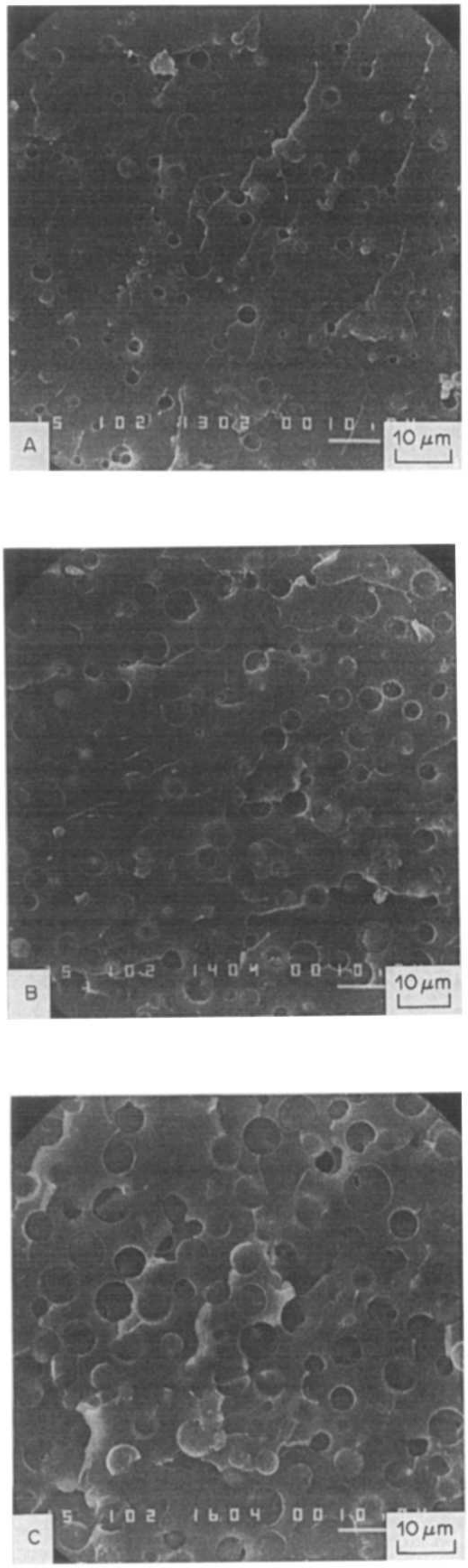


Fig. 8. Scanning electron micrographs (SEMs) of fracture surfaces for cured resins modified with terpolymer **Ia**. Amount of added **Ia**: (A) 10 wt%; (B) 20 wt%; (C) 30 wt%.

In the tan δ curve of the resin modified with **IIb**, increased elastomer content led to a gradual shift of the peak position of the α-relaxation towards lower temperature, a decrease in the magnitude of the α-relaxation and the emergence of a new broad relaxation at approx. 90° (Fig. 12). The storage modulus decreased gradually with increase in the terpolymer concentration (Fig. 13).

DISCUSSION

The use of elastomers **I** or **II** with pendant epoxy groups as modifiers was effective for improving the brittleness of the cured epoxy resins. The relative contents of BA and VBGE units in the elastomer are important to obtain more effective modifiers, because BA-rich elastomers tend to separate macroscopically in the cured system and VBGE-rich copolymers are likely to dissolve into the epoxy matrix phase [3]. The latter copolymers, moreover, have poor elastic properties. The present terpolymerization enabled us to control carefully both the fraction of BA units and the epoxy content of modifiers. The use of the higher molecular weight elastomer ($\bar{M}_n$ 22,300) led to micro-separated structure in which the large elastomer particles were dispersed in the epoxy matrix (Table 2). The acrylic terpolymers of lower $\bar{M}_n$ (8200–10,500) resulted in increased toughness of the epoxy resin at some expense of mechanical properties of the resin. This result indicates that the molecular weight of the elastomer also plays an important role in the modification. The toughening mechanism can be explained in terms of the morphological and dynamic mechanical behaviour.

The morphological examination gave interesting information on the micro-structure of the cured resins modified with the terpolymers. The results in Table 2 indicate that the St-containing terpolymer **Ia** with the lower BA content (62 mol%) dissolved partially in the epoxy matrix phase whereas most of **Ib** containing more BA units (74 mol%), except for the concentration of 30 wt%, formed the dispersed particles without dissolving in the epoxy matrix phase. In the addition of 30 wt% elastomer **Ib**, it dissolved partially in the epoxy matrix phase as shown by dynamic mechanical analysis (see later). These morphological behaviours correspond to the toughness of the cured epoxy resins. The fracture toughness for the cured resin modified with **Ib** was larger than that modified with **Ia** at an elastomer concentration of 10–20 wt%. On addition of 30 wt% of **Ib**, however, K_{Ic} decreased abruptly owing to larger dispersed particle size (10.2 μm) in the cured system. The K_{Ic} for modification with **Ia** increased with increase in the elastomer content, in spite of increase of particle size (see Fig. 3 and Table 2). It is interesting that the particle size is independent of the composition and concentration of terpolymer in the case of the most suitable conditions for modification. Particle size in the range of 4.5–5.9 μm would be suitable to improve the brittleness of the cured resin in the present system.

The compatibility of AN-containing elastomer **II** with the parent epoxy resin is higher than that of St-containing elastomer **I**. This effect might be explained by the solubility parameters (SP) of the

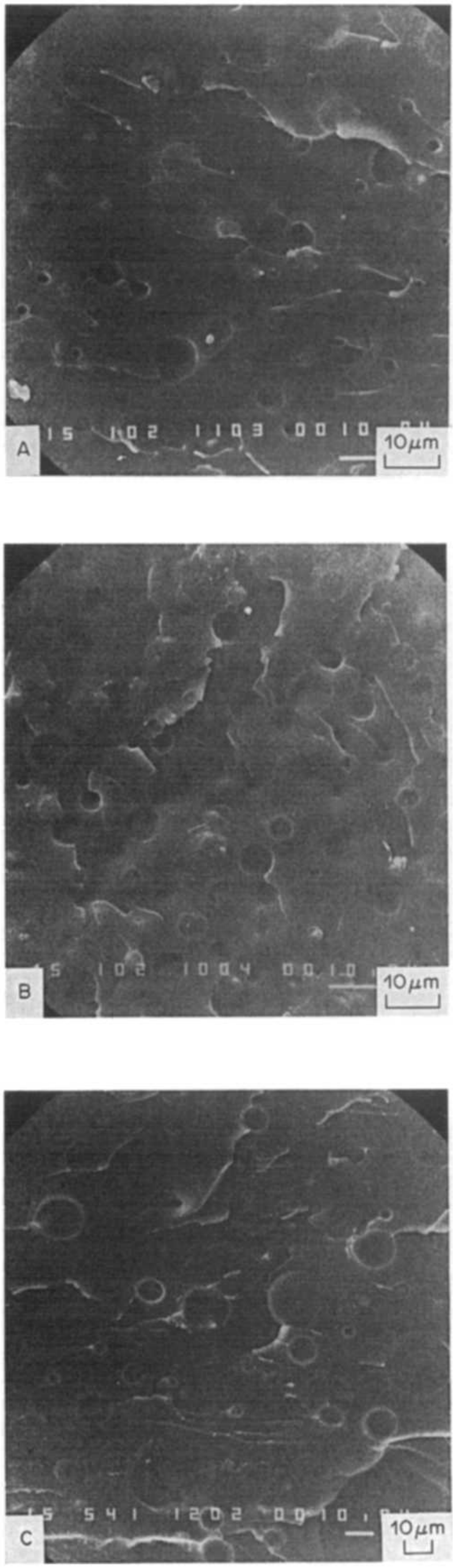


Fig. 9. SEMs of fracture surfaces for cured resins modified with **Ib**. Amount of added **Ib**: (A) 10 wt%; (B) 20 wt%; (C) 30 wt%.

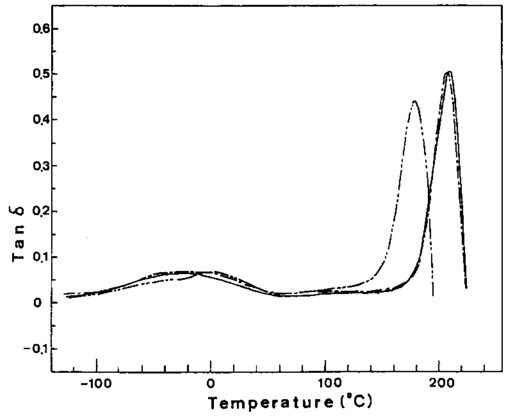


Fig. 10. Temperature dependence of tan δ for cured resins modified with **Ib**. (——) Parent epoxy resin; (— — —) 20% addition; (—·—·—) 30 wt% addition.

elastomers (see Table 1). It has been reported [3] that there is high compatibility between the epoxy resin and BA/VBGE elastomers containing 45 mol% of VBGE units. In the modification of epoxy resins with carboxyl-terminated butadiene–acrylonitrile rubber (CTBN) [6], increase in the AN content of the modifier resulted in decreased volume fraction and diameter of the dispersed domain.

The results obtained by dynamic mechanical analysis correspond to the morphologies of the cured resins. The tan δ curve for the cured resin, modified with 10–20 wt% of the St-containing terpolymer, was similar to that for the parent epoxy resin except for an increase in low temperature relaxation around 0°. An increase in the K_{1c} values for the cured resins modified with 10–20 wt% of **Ib** can be correlated with the low temperature relaxation. Such a correlation of low temperature relaxation height (or area) with the toughness of the cured resin has been reported in the modification of epoxy resins with CTBN [6]. On the addition of 30 wt% of **Ib**, the K_{1c} value decreased considerably owing to the larger dispersed particles (Table 2 and Fig. 3). It is noteworthy that there is a significant difference between the addition of 20 and 30 wt% of elastomer **Ib** in dynamic mechanical behaviour. Such behaviour corresponds to the morphology and the toughness of the cured resin. The large shift of α-relaxation after modification with 30 wt% of **Ib** shows that part of **Ib** dissolves into the epoxy matrix phase. A decrease in relaxation at $-45°$ might be the result of the inclusion of the epoxy component into the dispersed particle.

There is a gradual shift of α-relaxation and the appearance of the new broad relaxation around 95° in the modification with the AN-containing terpolymer. This new relaxation can be attributed to the formation of a matrix phase composed of the parent epoxy and dissolved **II** as seen in the morphological behaviour. These behaviours can be explained by the high compatibility of the parent epoxy resin and AN-containing **II** (see Table 1).

Toughening cured epoxy resins by elastomers must satisfy two requirements [7]. The first is compatibility and the elastomers must separate microscopically in the cured resins. The importance of such microphase

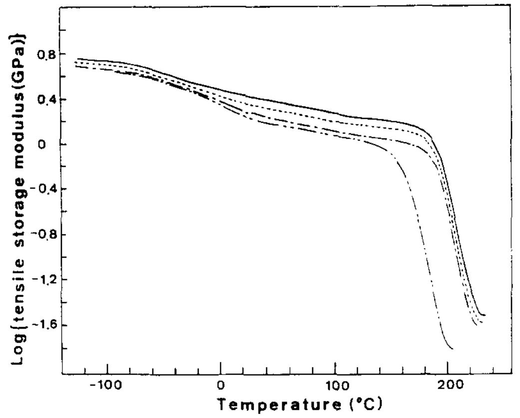


Fig. 11. Temperature dependence of storage modulus, E', for cured resins modified with **Ib**. (——) Parent epoxy resin; (-----) 10 wt% addition; (— — —) 20 wt% addition; (— - — -) 30 wt% addition.

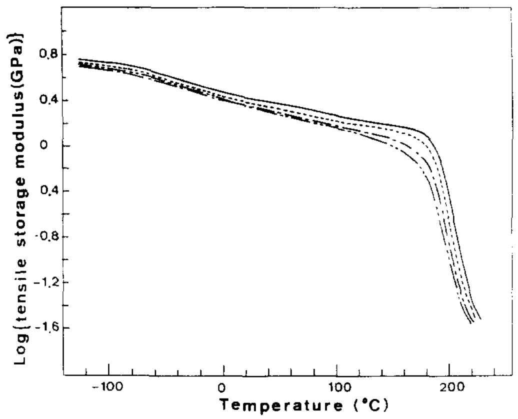


Fig. 13. Temperature dependence of storage modulus, E', for **IIb**-modified cured resins. (——) Parent epoxy resin; (-----) 10 wt% addition; (— — —) 20 wt% addition; (— - — -) 30 wt% addition.

separation has been reported for the modification of epoxy resins with reactive elastomers such as CTBN [8].

The microphase separations of the acrylic elastomer modified resins, examined by SEMs, indicated that the St-containing terpolymers dispersed to a greater extent than the AN-containing materials (Fig. 8). The second requirement is an interfacial bonding between two uncompatibilized phases. Reactive rubbers are also useful for this purpose. It has been reported [3] that pendant epoxy groups of acrylic elastomers are important in the toughening of the network because of the covalent bonding of the epoxy matrix phase with the epoxy group of the dispersed elastomer particles. The St-containing terpolymer modified resin is thought to satisfy these two requirements better than the AN-containing system.

In conclusion, modification of the cured epoxy resin with the acrylic terpolymers can increase the toughness of the resin at minimal expense of mechanical properties. The terpolymers containing St units were more effective as modifiers. The most suitable composition for the modification of the epoxy resin was inclusion of 20 wt% of the terpolymer containing 74 mol% BA, 18 mol% VBGE and 8 mol% St units.

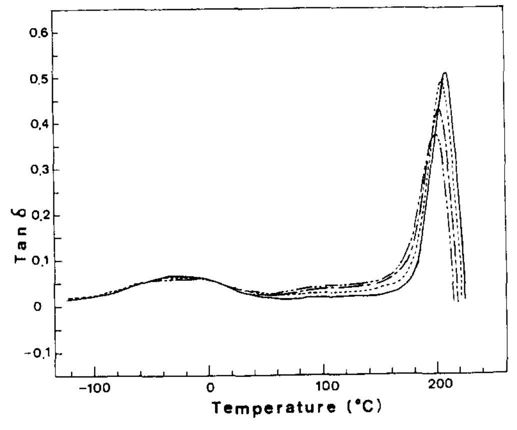


Fig. 12. Temperature dependence of tan δ for IIb-modified cured resins. (——) Parent epoxy resin; (-----) 10 wt% addition; (— — —) 20 wt% addition; (— - — -) 30 wt% addition.

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