

Internal Stress of Epoxy Resin Modified with Acrylic Core-shell Particles Containing Functional Groups Prepared by Seeded Emulsion Polymerization

YOSHINOBU NAKAMURA, HARUO TABATA, HIDETO SUZUKI, and KAZUO IKO, *Electrotechnical Research Laboratory, Nitto Electric Industrial Co., Ltd., Shimohozumi, Ibaraki, Osaka 567 Japan* and MASAYOSHI OKUBO and TSUNETAKA

MATSUMOTO, *Department of Industrial Chemistry, Faculty of Engineering, Kobe University, Rokko, Nada-ku, Kobe 657, Japan*

Synopsis

In order to reduce the internal stress in a cured epoxy resin, submicrometer-sized poly(butyl acrylate) (PBA)/poly(methyl methacrylate) (PMMA) core-shell particles having cross-links were dispersed in the resin prior to curing. For the introduction of cross-links, monoethylene glycol dimethacrylate or glycidyl methacrylate monomer was copolymerized. Cross-links in the PBA core reduced the shrinkage of the cured epoxy resin, and cross-links at the PMMA shell produced a strong interaction with the epoxy matrix. The internal stress was reduced effectively by the introduction of cross-links.

INTRODUCTION

Epoxy resin is widely used in the fields of coatings, adhesives, castings, materials for electrical insulators, and others. It is well known that the internal stress in epoxy resins cured at high temperature is produced by the shrinkage occurring in the cooling process from cure temperature to room temperature.¹⁻³ The internal stress reduces adhesion strength and occasionally induces cracks in the casting materials.⁴⁻⁶ In a previous article,⁷ in order to reduce the internal stress, submicrometer-sized soft polymer particles were dispersed in the resin prior to curing. For this purpose, four kinds of poly(butyl acrylate) (PBA)/poly(methyl methacrylate) (PMMA) core-shell particles were prepared by seeded emulsion polymerization for methyl methacrylate (MMA) with PBA seed particles with different particle diameters and subsequently were powdered by drying at room temperature. In the dispersion system, it was observed by scanning electron microscopy (SEM) that the PBA core were dispersed as domains in the cured epoxy matrix. The PMMA shell, which was needed to obtain the PBA/PMMA core-shell particles in the powder state, seemed to dissolve in the matrix. As was expected, the internal stress was decreased by modification with the particles. The relationship between the domain size and the internal stress was discussed in detail.

The aim of this work is to clarify the effect on the reduction of internal stress of the introduction of functional groups in the particles for the purpose

TABLE I
 Recipes for Emulsion Polymerization^a

Emulsion no.	1	2	3	4	5	6	7	8	9	10	11
Emulsion 1 (g)	—	26.0	—	—	—	—	—	—	—	—	—
Emulsion 2 (g)	—	—	28.7	—	—	—	—	—	—	—	—
Emulsion 3 (g)	—	—	—	26.5	—	26.5	—	—	26.5	—	—
Emulsion 4 (g)	—	—	—	—	49.0	—	—	—	—	—	—
Emulsion 6 (g)	—	—	—	—	—	—	48.3	48.3	—	—	—
Emulsion 9 (g)	—	—	—	—	—	—	—	—	—	50.3	50.3
<i>n</i> -Butyl acrylate (g)	40.0	35.0	—	35.0	—	32.8	—	—	32.0	—	—
Glycidyl methacrylate (g)	—	—	—	—	—	2.2	—	0.5	—	—	—
Monoethylene glycol dimethacrylate (g)	—	—	—	—	—	—	—	—	3.0	—	0.7
Methyl methacrylate (g)	—	—	—	—	6.7	—	6.7	6.2	—	6.7	6.0
Potassium persulfate (g)	0.24	0.21	0.21	0.21	0.04	0.21	0.04	0.04	0.21	0.04	0.04
Water (g)	160	139	136	139	111	130	112	112	130	110	110
Time (h)	6	6	6	6	6	6	6	6	6	6	6
Polymer concentration (%)	19.2	17.4	18.9	20.4	9.2	20.7	8.9	9.3	19.9	9.7	9.5
Particle diameter (μm)	0.22	0.32	0.58	1.10	1.20	1.10	1.08	1.21	1.05	1.15	1.16
					± 0.15		± 0.20	± 0.18		± 0.17	± 0.15

^a Polymerization temperature, 70°C. Atmosphere, N₂.

of developing strong interactions at the interfacial layer between the domains and the epoxy matrix.

EXPERIMENTAL

Materials

The epoxy resin used was a bisphenol-A epoxy resin (Epikote 828, Shell Chemical Co.; equivalent weight per epoxy group, 190 ± 5 ; average molecular weight, 380). 2,4,6-Tris(dimethyl aminomethyl)phenol (DMP-30) was used as an accelerator for curing the epoxy resin. *n*-butyl acrylate (BA) and MMA were purified by distillation under reduced pressure in a nitrogen atmosphere and stored in a refrigerator. Analytic-grade potassium persulfate was used as initiator, and commercial-grade glycidyl methacrylate (GMA) and monoethylene glycol dimethacrylate (1G) monomers were used without further purification.

Seeded Emulsion Polymerization

Table I shows recipes for emulsion polymerizations. PBA emulsion (emulsion 4) and P(BA-GMA) emulsion (emulsion 6) were prepared by seeded emulsion polymerization for BA and BA-GMA with PBA seed particles (emulsion 3), respectively. The molar ratio of BA-GMA was 95:5. Next, the seeded emulsion polymerizations for MMA and MMA-GMA (95:5 molar ratio) were carried out with PBA (emulsion 4) or P(BA-GMA) (emulsion 6) particles as seed under the conditions of emulsions 5, 7, and 8, respectively. The ratio BA (or BA-GMA)-MMA (or MMA-GMA) was 60:40 (w/w). The total amount of monomers in the seeded emulsion polymerizations was collectively added to the flask just before the polymerization was started. As described in earlier articles,^{7,8} emulsions 5, 7, and 8 of polymer particles should have a core-shell structure consisting of PBA-rich core and PMMA-rich shell.

TABLE II
Formulation of Modified Epoxy Resin

	Unmodified (phr) ^a	Modified (phr)
Epoxy resin	100	100
PBA/PMMA emulsion particles (powder)	—	16.7 (core polymer ^b = 10 phr)
DMP-30	4	4

^a Parts per hundred resin by weight.

^b PBA, P(BA-GMA), and P(BA-1G).

Moreover, in place of the GMA component, the polymer particles containing the 1G component (emulsions 10 and 11) were produced by the same emulsion polymerization technique. All polymerizations were continued until the conversion attained was above 98%. After the polymerizations, each emulsion was filtrated with cheese-cloth of 100 mesh. Particle diameter was determined with SEM. Average particle diameters of PBA, P(BA-GMA) and P(BA-1G) seed emulsions (emulsions 4, 6, and 9) were calculated from the measured diameter of corresponding core-shell particles [emulsions 5, 7 (8), and 10 (11), respectively], based on the polymerization recipes. Powders of emulsions 5, 7, 8, 10, and 11 were obtained by drying each emulsion at room temperature.

Modification of Cured Epoxy Resins with Polymer Particles

Table II shows the formulations of the modified epoxy resins. The powder of polymer particles and the accelerator were added to the epoxy resin and hand-mixed by spatulas at room temperature for 10 min. The total quantity of these materials was approximately 5 g. The mixture was coated on an aluminum plate (15 × 90 mm; thickness, 0.2 mm). The coating thickness was about 0.1 mm. The coated aluminum plates were placed at 80°C for 2 h and then at 180°C for 4 h.

Internal Stress

When the coated aluminum plates were cooled to room temperature, they curved, owing to the difference in the linear thermal expansion coefficients between the aluminum plate and the cured epoxy resin. The internal stress was calculated by the same method,^{9,10} described in detail in the previous article.⁷

Measurements

Linear thermal expansion coefficients of the cured epoxy resins and the dynamic mechanical properties were measured by the same method described in the previous article.⁷

RESULTS AND DISCUSSION

In order to form a strong interaction at the interfacial layer between the domains and the matrix, the functional groups were introduced into the core part of particles by copolymerization of the GMA or 1G component with BA.

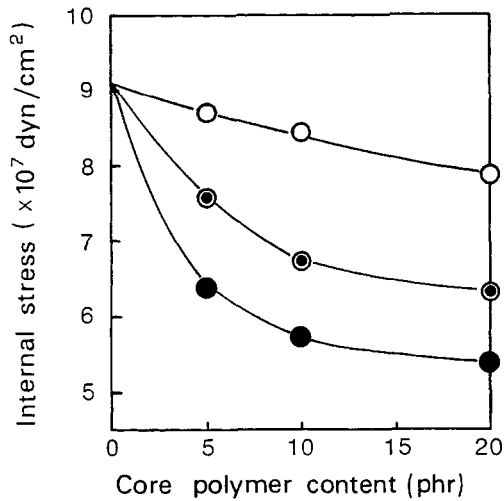


Fig. 1. Effect of presence [P(BA-GMA)/PMMA, ○; P(BA-GMA)/P(MMA-GMA), ●] or absence (PBA/PMMA, ○) of glycidyl methacrylate (GMA) component in various core-shell polymer particles on the internal stress of cured epoxy resins modified with the particles.

The polymer components of the core part, PBA, P(BA-GMA), and P(BA-1G), aid the flexibility of the epoxy resin. The PMMA shell should dissolve as described in the previous article.⁷ Epoxy groups derived from GMA should react with those of matrix at the interfacial layer, whereas with 1G, so-called interpenetrating polymer networks (IPN)¹¹ should be formed at the interfacial layer between the two networks.

Figure 1 shows the result with GMA component. As is obvious in comparing PBA/PMMA and P(BA-GMA)/PMMA, the introduction of GMA compo-

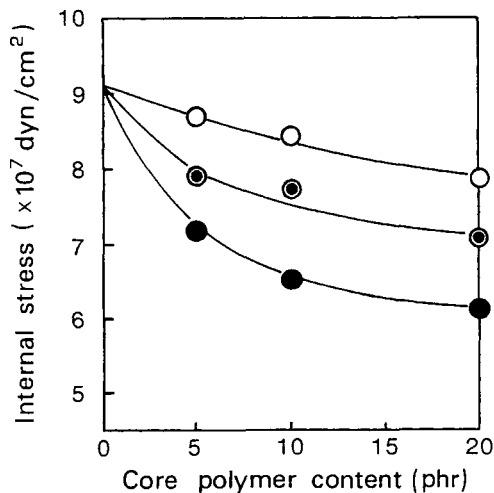


Fig. 2. Effect of presence [P(BA-1G)/PMMA, ○; P(BA-1G)/P(MMA-1G), ●] or absence (PBA/PMMA, ○) of monoethylene glycol/ dimethacrylate (1G) component in various core-shell polymer particles on the internal stress of cured epoxy resins modified with the particles.

nent into the core (domains) reduced the internal stress. The same result was also obtained with the P(BA-1G)/PMMA particles, as shown in Figure 2. In the both systems, the core (domain) sizes were kept at the same value as listed for emulsions 4 and 6 in Table I, in order to neglect the effect of size on internal stress, which was discussed in detail in the previous article.⁷

These results indicate that the strong interaction at the interfacial layer obviously enhances the effect of modification with soft polymer particles on the reduction of internal stress. There is a possibility that internal stress is reduced by cross-links, not only at the interfacial layer but also in the interior of domains. This point will be discussed later.

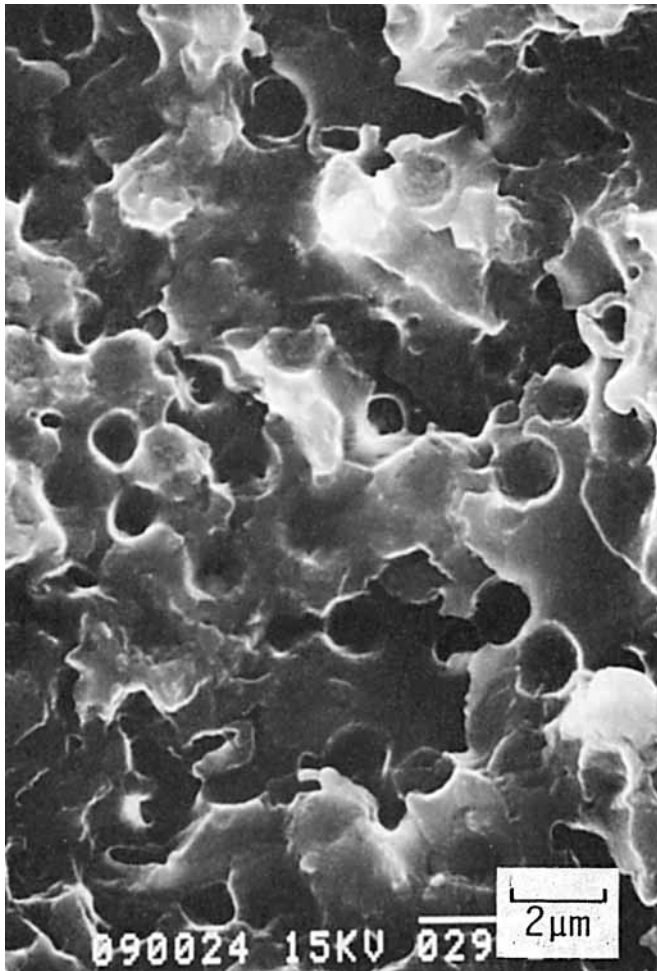
As shown in Figures 1 and 2, P(BA-GMA)/P(MMA-GMA) and P(BA-1G)/P(MMA-1G) were more effective in the reduction of internal stress than P(BA-GMA)/PMMA and P(BA-1G)/PMMA, respectively. Shells of the former, which consist of P(MMA-GMA) or P(MMA-1G), seem to remain at the interface between the soft polymer domains and the cured epoxy matrix. The interfacial layer composed of the MMA component has a Young's modulus intermediate between that of the domain and that of the matrix. Accordingly, it may be effective to smoothly transfer the stress in the matrix to the soft domains.

Figure 3a, b, and d shows the morphologies of the fracture surfaces of epoxy resins modified with PBA/PMMA, P(BA-GMA)/P(MMA-GMA), and P(BA-1G)/P(MMA-1G) particles observed by SEM. In the epoxy resin modified with PBA/PMMA particles (Fig. 3a), a heterogeneous structure with PBA particles independently dispersed in the epoxy resin was clearly observed, although such clear interfaces were not observed in systems modified with P(BA-GMA)/P(MMA-GMA) (Fig. 3b) or P(BA-1G)/P(MMA-1G) (Fig. 3d) particles. This demonstrates that the compatibility between polymer particles and the epoxy matrix was apparently increased by the introduction of the GMA or 1G component in the shell layer.

Table III shows some properties of these modified epoxy resins. Linear thermal expansion coefficients α_1 of the epoxy resins modified with P(BA-GMA)/P(MMA-GMA) or P(BA-1G)/P(MMA-1G) particles in a glassy state below the glass transition temperature T_g of the epoxy resin were smaller than with PBA/PMMA particles. The complex modulus E_c at room temperature of epoxy resins modified with particles containing 5 mol% of the GMA or 1G component was equal to that with PBA/PMMA particles. These results indicate that the greater reduction of internal stress observed with P(BA-GMA)/P(MMA-GMA) and P(BA-1G)/P(MMA-1G) than with PBA/PMMA may be derived from the decrease in α_1 because the internal stress is expressed by multiplication of E_c and α_1 . This decrease may be the reason that the degree of expansion of polymer segments in particles with heating is suppressed by cross-links. To examine these results further, P(BA-1G)/P(MMA-1G) particles with various 1G contents (2–20 mol%) in both core and shell were dispersed in the epoxy resin.

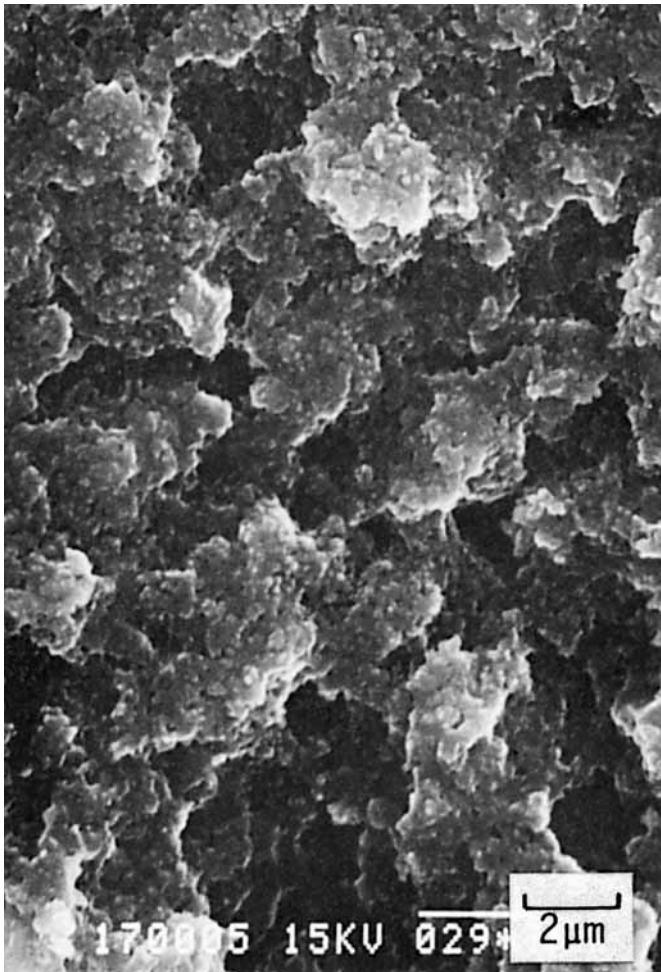
Figure 4 shows that, with increasing 1G content, the internal stress decreased up to 5 mol% and then increased. Thus there was an optimum 1G content to minimize internal stress.

Figure 3c–f shows the morphologies of the fracture surfaces of the epoxy resin modified with these polymer particles observed by SEM. In 1G contents



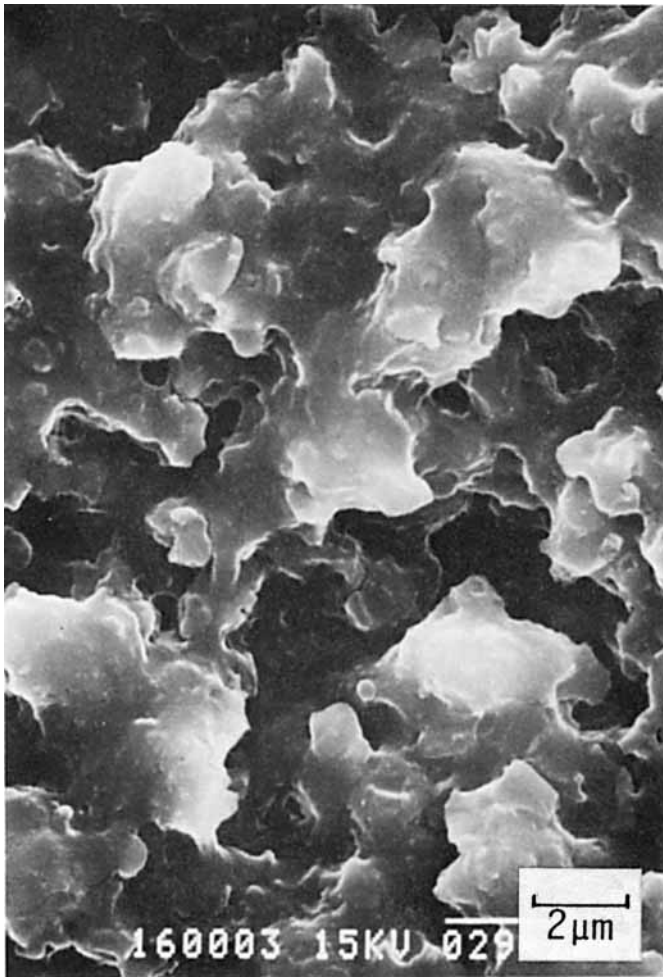
(a)

Fig. 3. Fracture surfaces of cured epoxy resins modified with various polymer particles. (a) Modified with PBA/PMMA core-shell particles. (b) Modified with P(BA-GMA)/P(MMA-GMA) core-shell particles: glycidyl methacrylate (GMA) contents = 5 mol%. (c) Modified with P(BA-1G)/P(MMA-1G) core-shell particles: monoethylene glycol dimethacrylate (1G) content = 2 mol%. (d) Modified with P(BA/1G)/P(MMA-1G) core-shell particles: 1G content = 5 mol%. (e) Modified with P(BA/1G)/P(MMA-1G) core-shell particles: 1G content = 10 mol%. (f) Modified with P(BA-1G)/P(MMA-1G) core-shell particles: 1G content = 20 mol%.



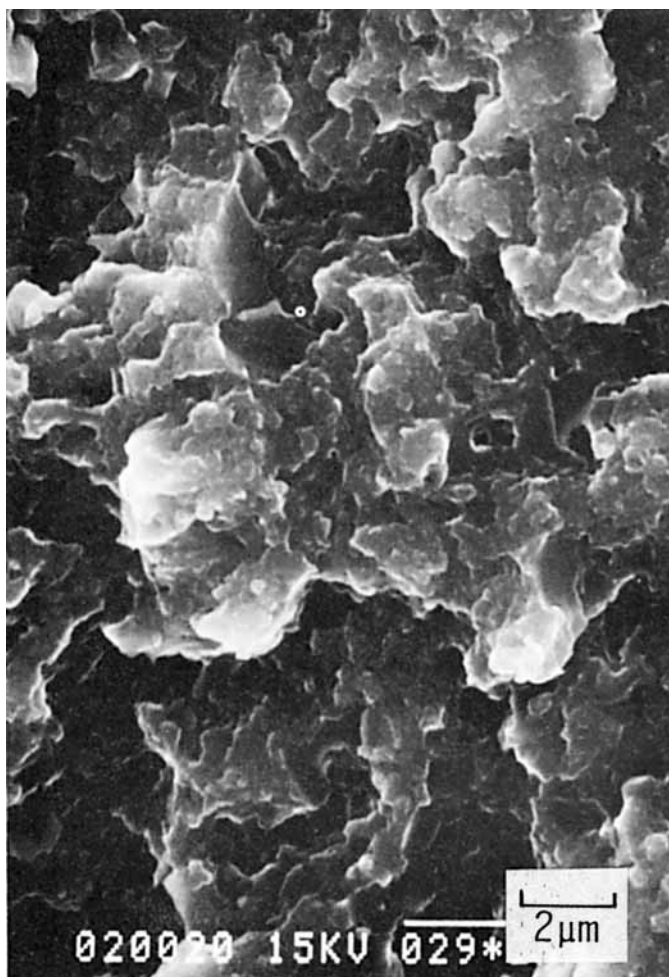
(b)

Fig. 3. (Continued from the previous page.)



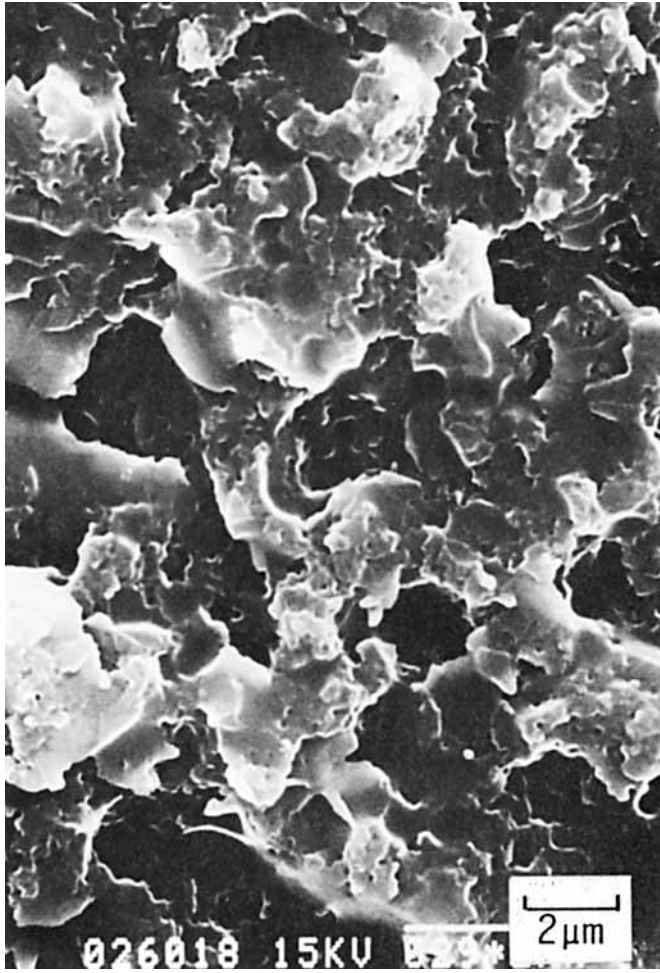
(c)

Fig. 3. (Continued from the previous page.)



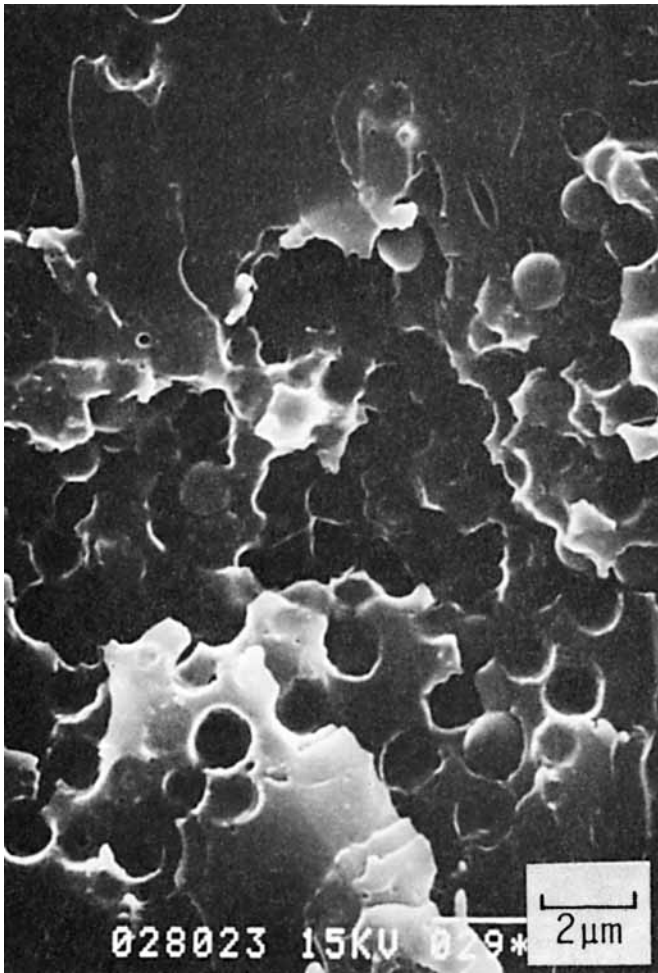
(d)

Fig. 3. (Continued from the previous page.)



(e)

Fig. 3. (Continued from the previous page.)



(f)

Fig. 3. (Continued from the previous page.)

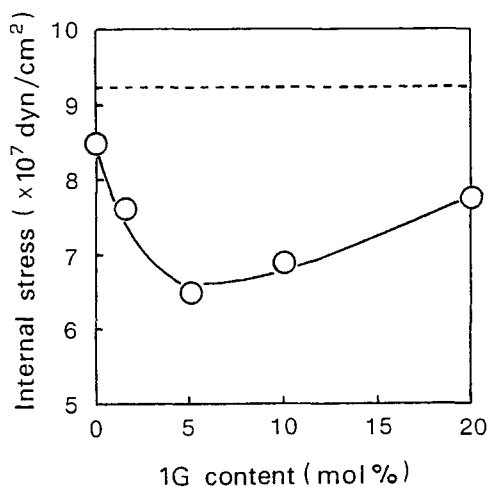


Fig. 4. Effect of monoethylene glycol dimethacrylate (1G) content in P(BA-1G)/P(MMA-1G) core-shell polymer particles on the internal stress of cured epoxy resins modified with the particles. The broken line indicates the internal stress value of unmodified cured epoxy resin.

TABLE III
Some Properties of Cured Modified Epoxy Resins

Core part Shell layer	Unmodified	Modified ^a		
	—	PBA PMMA	P(BA-GMA) P(MMA-GMA)	P(BA-1G) P(MMA-1G)
α_1 ($\times 10^{-5}/^{\circ}\text{C}$) ^b	7.9	8.2	6.2	7.3
E_c ($\times 10^{10}$ dyn/cm ²) ^c	2.0	1.6	1.6	1.6
T_g ($^{\circ}\text{C}$) ^d	130	130	130	130
Internal stress ($\times 10^7$ dyn/cm ²)	9.2	8.5	5.7	6.5

^a Modified with various core-shell particles. Core polymer content = 10 phr.

^b Linear thermal expansion coefficient of epoxy resin in glassy state.

^c Complex modulus at 25 $^{\circ}\text{C}$ obtained from dynamic mechanical measurement.

^d Temperature at peak of $\tan \delta$.

TABLE IV
Some Properties of Cured Modified Epoxy Resins

	Unmodified	Modified, ^a 1G content (mol%)				
		0	2	5	10	20
α_1 ($\times 10^{-5}/^{\circ}\text{C}$) ^b	7.9	8.2	7.6	7.3	7.1	6.8
E_c ($\times 10^{10}$ dyn/cm ²) ^c	2.0	1.6	1.6	1.6	1.6	1.8
T_g ($^{\circ}\text{C}$) ^d	130	130	130	130	130	130
Internal stress ($\times 10^7$ dyn/cm ²)	9.2	8.5	7.7	6.5	6.9	7.8

^a Modified with P(BA-1G)/P(MMA-1G) core-shell particles. Core polymer content = 10 phr.

^b Linear thermal expansion coefficient of epoxy resin in a glassy state.

^c Complex modulus at 25 $^{\circ}\text{C}$ obtained from dynamic mechanical measurement.

^d Temperature at peak of $\tan \delta$.

from 2 to 10 mol%, the surfaces of holes due to the falling away of particles were not smooth. At 0 and 20 mol% 1G content, the surfaces were also smooth (Fig. 3a).

Table IV shows some properties of these modified epoxy resins. With increasing 1G content, α_1 decreased gradually. The E_c at room temperature were the same in the range from 0 to 10 mol% and somewhat high at 20 mol%.

The T_g , which was determined as the temperature at the peak of $\tan \delta$ of the epoxy resins in all modified systems, were the same as that of unmodified systems, as shown in Tables III and IV. This indicates that the modification applied in this article may reduce the internal stress without lowering the thermal resistance of the epoxy resin.

From these results, it is concluded that the cross-links introduced in both core and shell operate as follows, resulting in the reduction of the internal stress of the modified epoxy resin: cross-links in the core reduce the α_1 ; cross-links at the shell produce strong interaction with the epoxy matrix due to the formation of IPN. However, when cross-links are too tight to form IPN because of inhibition of mutual diffusion of segments at the interfacial layer, the reduction is weak. Thus, there is an optimum number of cross-links for the reduction of internal stress.

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