

# Internal Stress of Epoxy Resin Modified with Acrylic Core-Shell Particles Prepared by Seeded Emulsion Polymerization\*

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## Synopsis

In order to reduce the internal stress in a cured epoxy resin, the submicron polymer particles were dispersed therein prior to curing. For this purpose, four kinds of poly(butyl acrylate)/poly(methyl methacrylate) core-shell particles were prepared by seeded emulsion polymerization for methyl methacrylate with poly(butyl acrylate) seed particles having different particle diameter, and subsequently were powdered by drying at room temperature. It was observed by SEM that poly(butyl acrylate) particles as core were dispersed in the cured epoxy matrix. Poly(methyl methacrylate) as shell seems to dissolve in the matrix. The internal stress of cured epoxy resin decreased with the modification of the particles and the tendency was enhanced with a decreasing in the particle diameter.

## INTRODUCTION

Since an epoxy resin has excellent solvent resistance, mechanical properties, good adhesion to many substrates, and electrical properties, it is widely used in the fields of coatings, adhesives, castings, materials for electrical insulators, etc. 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 the cure temperature to room temperature.<sup>1-3</sup> The internal stress reduces adhesion strength and occasionally induces cracks in the casting materials.<sup>4-6</sup> Previously, there are some researches in which reducing the internal stress by modification of epoxy networks was tried with such a functional liquid rubber as carboxy-terminated butadiene-acrylonitrile copolymer.<sup>7-9</sup> In these cases, the modified epoxy resins had heterogeneous structure that the elastomer were dispersed as domains in the continuous phase of epoxy resin. However, to our knowledge, the effect of the domain size on the internal stress of modified epoxy resins has not been clarified. It is the reason why the controls of the domain size and of its distribution without changing other functions is very difficult experimentally.

Therefore, this work was undertaken to clarify it. For this purpose poly(butyl acrylate) (PBA)/poly(methyl methacrylate) (PMMA) core-shell particles having different core sizes prepared by seeded emulsion polymerization were dispersed in the epoxy resin, respectively. PBA-core is expected to be available

as a flexibilizer for the epoxy resin and PMMA-shell should be useful to make a powder state which is needed to disperse PBA-core independently in the epoxy resin.

## EXPERIMENTAL

### Materials

The epoxy resin used was bisphenol-A-type epoxy resin (Epikote 828, Shell Chemical Co., equivalent weight per epoxy group:  $190 \pm 5$ , average molecular weight: 380). 2,4,6-Tris(dimethyl aminomethyl)phenol (DMP-30) was used as an accelerator for curing of epoxy resin. Butyl acrylate (BA) and methyl methacrylate (MMA) were purified by distillation under reduced pressure in a nitrogen atmosphere and stored in a refrigerator. Analytical-grade potassium persulfate was used as initiator without further purification.

### Seeded Emulsion Polymerization

Table I shows the recipes of emulsion polymerizations. Four kinds of PBA emulsion (nos. 1–4) having different particle diameter were prepared stepwisely by using seeded emulsion polymerization technique. Next, the seeded emulsion polymerizations for MMA were carried out with above PBA particles as seed under the conditions of nos. 5–8, respectively. The ratio of BA/MMA was 60/40 (w/w). The total amount of monomer (BA or MMA) in the seeded emulsion polymerizations was collectively added to the flask just before the polymerization is started. As described in an earlier article,<sup>10</sup> nos. 5–8 polymer particles should have core-shell structure consisting of PBA-rich core and PMMA-rich shell. All polymerizations were continued until the conversion attained above 98%. Particle diameter was determined with a scanning electron microscope (SEM) (Hitachi Ltd., S-450). Average particle

TABLE I  
Recipes of Emulsion Polymerization<sup>a</sup>

Sample no.	1	2	3	4	5	6	7	8
No. 1 emulsion (g)	—	26.0	—	—	52.1	—	—	—
No. 2 emulsion (g)	—	—	28.7	—	—	57.5	—	—
No. 3 emulsion (g)	—	—	—	26.5	—	—	52.9	—
No. 4 emulsion (g)	—	—	—	—	—	—	—	49.0
BA <sup>b</sup> (g)	40.0	35.0	35.0	35.0	—	—	—	—
MMA <sup>c</sup> (g)	—	—	—	—	6.7	6.7	6.7	6.7
KPS <sup>d</sup> (g)	0.24	0.21	0.21	0.21	0.04	0.04	0.04	0.04
Water (g)	160	139	136	139	108	103	108	111
Time (g)	6	6	6	6	6	6	6	6
Polymer concn (%)	19.2	17.4	18.9	20.4	9.4	9.5	9.7	9.2
Particle diameter ( $\mu\text{m}$ )	0.22	0.32	0.58	1.10	0.24 $\pm 0.03$	0.35 $\pm 0.05$	0.63 $\pm 0.10$	1.20 $\pm 0.15$

<sup>a</sup> Polymerization temp: 70°C. Atmosphere: N<sub>2</sub>.

<sup>b</sup> Butyl acrylate.

<sup>c</sup> Methyl methacrylate.

<sup>d</sup> Potassium persulfate.

diameters of PBA seed emulsions (nos. 1-4) were calculated from the measured diameter of corresponding PBA/PMMA core-shell particles (nos. 5-8) based on the polymerization recipes, respectively. Actually, powders of nos. 5-8 could be obtained by drying each emulsion at room temperature, respectively.

### 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 amount of these materials were ca. 5 g. The mixture was coated on an aluminum plate (15 × 90 mm, thickness: 0.2 mm). The coating thickness was ca. 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, it curved due to the difference of the linear thermal expansion coefficients between the aluminum plate and the cured epoxy resin. As illustrated in Figure 1, the coated aluminum plate was placed on the two shape knife edges with the distance  $l$  of 8 cm. The deviation  $\delta$  was measured by a reading scope and the radius of curvature,  $\rho$ , of the coated aluminum plate was

TABLE II  
Formulation of Modified Epoxy Resin

	Unmodified (phr) <sup>a</sup>	Modified (phr) <sup>a</sup>
Epoxy resin	100	100
PBA/PMMA emulsion particles (powder)	—	16.7 (PBA = 10)
DMP-30	4	4

<sup>a</sup> Parts per hundred resin by weight.

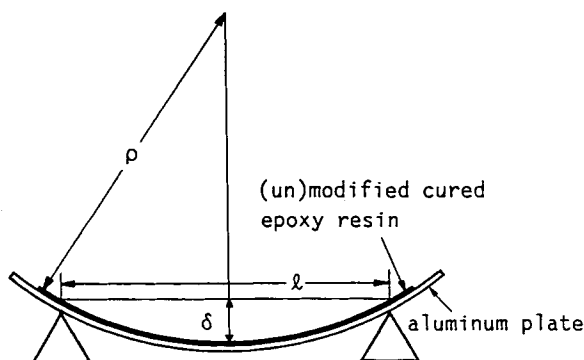


Fig. 1. Schematic view for the measurement of the curvature of the coated aluminum plate.

calculated by<sup>11,12</sup>

$$\rho = \frac{l^2}{8\delta} + \frac{\delta}{2} \doteq \frac{l^2}{8\delta} \quad (1)$$

The internal stress  $\sigma$  was calculated by<sup>11,12</sup>

$$\sigma = \frac{E_1 \cdot h_1^3}{12 \cdot h_2} \cdot \frac{2}{\rho \cdot H} \left[ 1 + \frac{1}{3} \left( \frac{h_1}{H} \right)^2 \right] \quad (2)$$

where  $E_1$  is Young's modulus of aluminum plate,  $h_1$  and  $h_2$  are thicknesses of aluminum plate and coated epoxy resin, respectively, and  $H = h_1 + h_2$ .

### Measurements

Linear thermal expansion coefficients of the cured epoxy resins were measured by thermal mechanical analysis (SSC/560M-type, Seiko Denshi Co.) with a heating rate of approximately 5°C/min. In this method, the length of the cured modified epoxy resin (thickness: 8 mm) was measured at different temperature below glass transition temperature ( $T_g$ ). Linear thermal expansion coefficients of the cured epoxy resins were calculated from the slope of the line in the relation between the temperature and the length. Dynamic mechanical properties were measured under tensile condition with Spectrometer (VES-FIII type, Iwamoto Co.) at 10 Hz with a heating rate of approximately 2°C/min. The morphologies of fracture surfaces of samples broken in liquid nitrogen were observed by SEM.

### RESULTS AND DISCUSSION

In this study, PBA ( $T_g = -54^\circ\text{C}$ )<sup>13</sup> was used as a flexibilizer for the epoxy resin. Since it is impossible to obtain the powder of PBA emulsion particles at room temperature because of coalescence, PBA/PMMA core-shell emulsion particles were used in this study. As already mentioned in experimental, they could be powdered by drying at room temperature because of the hardness of PMMA-shell.<sup>10</sup> The compatibility between the epoxy resin and PBA (and PMMA) was confirmed as follows. Each film (3 × 1 cm, thickness: 0.5 mm) of PBA and PMMA was dipped in the epoxy resin at 80°C for 48 h. PMMA film dissolved, whereas PBA film was only slightly swollen and became turbid. This suggests that PMMA-shell of PBA/PMMA particles should dissolve in the epoxy resin in the process of curing, whereas PBA-core should remain as a domain in the epoxy resin, independently.

Figure 2 shows the morphology of the fracture surfaces of modified epoxy resin with the polymer particles were observed by SEM. The heterogeneous structure which polymer particles were independently dispersed in the epoxy resin was clearly observed in the modified resins (b–e). The average domain sizes observed were approximately agreement with the calculated diameters of

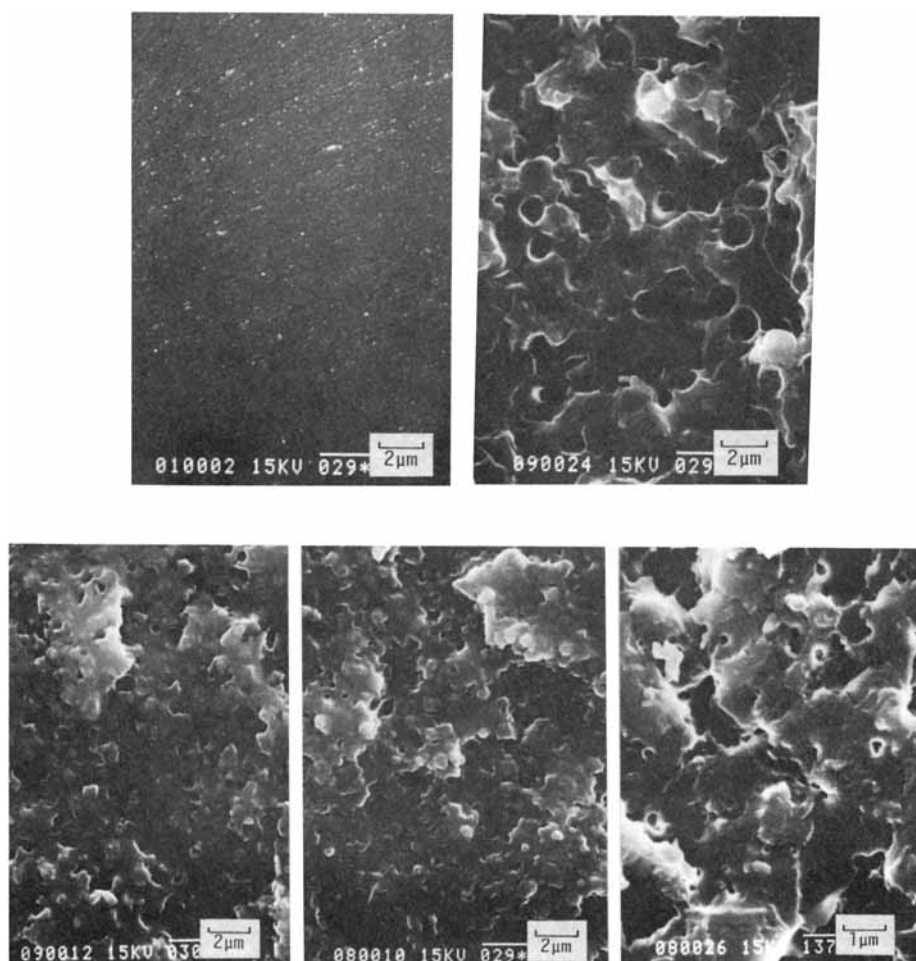


Fig. 2. Fracture surfaces of various cured epoxy resins modified with PBA/PMMA core-shell particles: (a) unmodified; (b) modified (PBA-core size:  $1.1 \mu\text{m}$ ); (c) modified (PBA-core size:  $0.58 \mu\text{m}$ ); (d) modified (PBA-core size:  $0.32 \mu\text{m}$ ); (e) modified (PBA-core size:  $0.22 \mu\text{m}$ ).

PBA seed particles as shown in Table I, respectively. This supports the above opinion that PMMA-shell dissolves in epoxy matrix in the process of curing. That is, it is concluded that the modification of the epoxy resin with PBA/PMMA core-shell particles is very available as the modified system for the purpose of clarifying the effect of size of soft domain on the internal stress.

Figure 3 shows the internal stress of the modified cured epoxy resins. The internal stress decreased with an increasing in PBA content as well as the case of the modification with rubber described in the introduction. In addition, the tendency was enhanced with a decreasing in PBA-core size.

Figure 4 shows the dynamic mechanical properties of the epoxy resins modified with two kinds of the polymer particles; PBA-core size: (A)  $0.22 \mu\text{m}$ ; (B)  $1.1 \mu\text{m}$ . In the case of  $1.1 \mu\text{m}$ , the sharp peaks of loss modulus ( $E''$ ) and  $\tan \delta$  for PBA which were observed at ca.  $-60^\circ\text{C}$ , respectively, were more

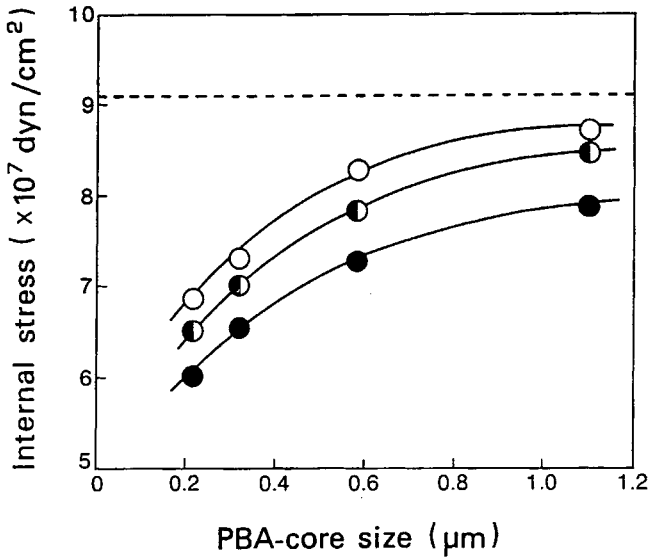


Fig. 3. Effect of PBA-core size on the internal stress of cured epoxy resins modified with PBA/PMMA core-shell particles; PBA content (phr): (○) 5; (◐) 10; (●) 20; (---) the internal stress value of unmodified cured epoxy resin.

broad than in the case of 0.22 μm. This indicates that the degree of mutual diffusion of segments at the interface between PBA domains and the epoxy matrix increases with an increasing in the total interfacial area due to the decrease in the size. This point seems to be important for the reduction of the internal stress and will be discussed in detail in a following article.

In general, under glassy state stress is expressed by multiplication of modulus and strain. This relation should be applied to the system mentioned

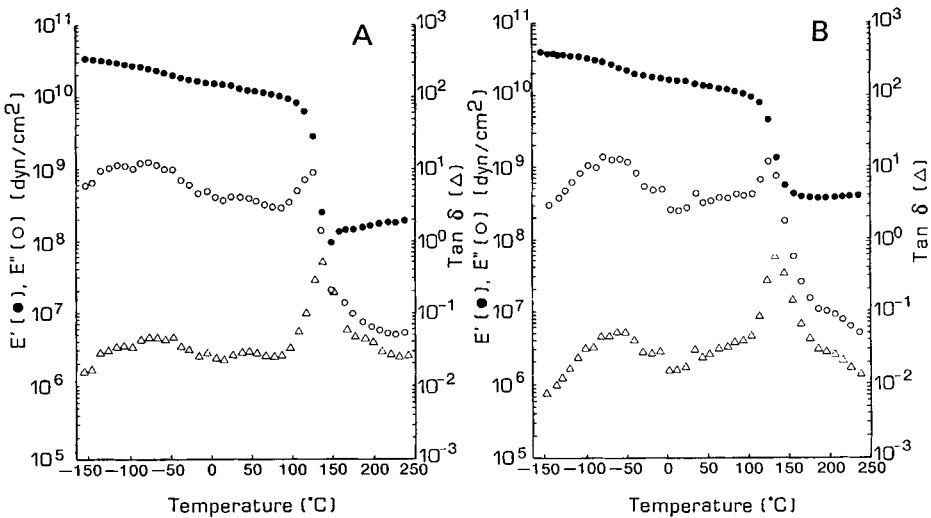


Fig. 4. Dynamic mechanical properties of cured epoxy resins modified with PBA/PMMA core-shell particles; PBA-core sizes: (A) 0.22 μm; (B) 1.1 μm.

TABLE III  
Some Properties of Cured Modified Epoxy Resins

PBA-core size	Unmodified	Modified <sup>a</sup>	
		0.22	1.1
$\alpha_1^b (\times 10^{-5}/^\circ\text{C})$	7.9	8.1	8.2
$E^c (\times 10^{10}\text{dyn}/\text{cm}^2)$	2.0	1.3	1.6
$T_g^d (^\circ\text{C})$	130	130	130
Internal stress ( $\times 10^7 \text{ dyn}/\text{cm}^2$ )	9.2	6.5	8.5

<sup>a</sup> Modified with PBA/PMMA core-shell particles. PBA/(epoxy resin + PMMA) = 10/90 (w/w).

<sup>b</sup> Linear thermal expansion coefficient of epoxy resin in glassy state.

<sup>c</sup> Complex modulus at 25°C obtained from dynamic mechanical measurement.

<sup>d</sup> Temperature at peak of  $\tan \delta$ .

above, wherein stress is internal stress and strain is shrinkage which corresponds to the linear thermal expansion coefficient.

Table III shows some properties of the unmodified epoxy resin and the above modified resins. Linear thermal expansion coefficients ( $\alpha_1$ ) of the modified epoxy resins in glassy state below  $T_g$  of the epoxy resin were nearly equal to that of unmodified resin, regardless of PBA-core size. Complex modulus decreased by modifying with the polymer particles and the tendency was enhanced with the decreasing in PBA-core size. These results indicate that the reduction of the internal stress is derived from the reduction of the modulus.

The  $T_g$ 's which were determined as the temperature at the peak of  $\tan \delta$  of these modified epoxy resins were same value as that of unmodified one. Therefore, it is concluded that the modification applied in this article could reduce the internal stress without a lowering of the thermal resistance of the epoxy resin.

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Received October 21, 1985

Accepted January 13, 1986