Internal Stress of Epoxy Resin Modified with Acrylic Polymers Produced by *In Situ* UV Radiation Polymerization

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Synopsis

A cured epoxy resin is modified with polybutyl acrylate (A) and polyethyl acrylate (B) produced by *in situ* ultraviolet radiation polymerizations of their corresponding monomers in the epoxy resin, respectively, to reduce the internal stress. In the A system, a heterogeneous structure with submicron domains was formed. In the B system, however, the B mixed well with the epoxy matrix. In both systems, the internal stress was decreased by the modification. The glass transition temperature of the epoxy matrix decreased in the B system more than in the A system. The A-modified resin was superior to the B-modified resin in reducing the internal stress without decreasing the thermal resistance of epoxy resin.

INTRODUCTION

Epoxy resin is widely used for coatings, adhesives, casting, electrical insulator material, and other applications. It is generally acknowledged that internal stress in epoxy resin cured at high temperature results from the shrinkage occurring in the cooling process between cure temperature and room temperature.[1-3] This internal stress reduces adhesive strength and occasionally causes cracks in the casting material.[4-6]

Previous research was aimed at reducing the internal stress in epoxy resin by modifying it with a functional liquid rubber such as carboxyl-terminated butadiene–acrylonitrile copolymer.[7-9] In that research, the modified epoxy resins had heterogeneous structures with the elastomer dispersed as domains in the epoxy matrix.

In a previous article,[10] we dispersed some kinds of poly(butylacrylate) (PBA)/poly(methyl methacrylate) (PMMA) core–shell particles in the epoxy matrix prior to curing. These particles are produced by seeded emulsion polymerization and powdered by drying at room temperature. Because the PMMA component dissolved in the epoxy matrix, only the PBA core remained as a soft domain in the epoxy matrix. Consequently, the domain size

could be controlled by using the PBA/PMMA particles having various PBA-core sizes. These particles are very useful models for studying the effects of the "soft" domain size on the internal stress. As a result, the internal stress was effectively reduced by decreasing in the PBA domain size. Further, by using the core–shell particles having functional groups, the reduction became more remarkable, because the interaction occurred at the domain/matrix interface.[11]

Sperling and co-workers prepared the materials consisting of the epoxy resin and PBA[12] [or poly(ethyl acrylate) (PEA)[13]] made by heat curing and *in situ* ultraviolet (UV) radiation polymerization, respectively. They treated it as interpenetrating polymer networks (IPN)[14] and measured the mechanical properties, but did not refer to the internal stress.

Therefore, in this study, we tried to reduce the internal stress of epoxy resin by introducing the uncrosslinked acrylic polymers using similar procedures.

EXPERIMENTAL

Materials

The epoxy resin used was bisphenol A type 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 in curing the epoxy resin. *n*-Butyl acrylate (BA) and ethyl acrylate (EA) were purified by distillation at reduced pressure in a nitrogen atmosphere and then stored in a refrigerator. Commercial grade benzyl dimethyl ketal (Irgacure 651, Ciba-Geigy) was used as a UV sensitive initiator.

In Situ UV Radiation Polymerization

Table I shows the formulations of the modified epoxy resins. BA (or EA) monomer, the UV sensitive initiator, and the accelerator were added to the epoxy resin and hand-mixed using a spatula at room temperature for 5 min.

TABLE I
Formulations of Modified Epoxy Resins[a]

Sample no.	1	2	3	4	5	6	7
	Unmodified			Modified			
Acrylic polymer	—	PBA	PBA	PBA	PEA	PEA	PEA
Epoxy resin[b]	100	100	100	100	100	100	100
BA[c] monomer	—	5	10	20	—	—	—
EA[d] monomer	—	—	—	—	5	10	20
UV sensitive initiator[e]	—	0.03	0.06	0.12	0.03	0.06	0.12
Accelerator[f]	4	4	4	4	4	4	4

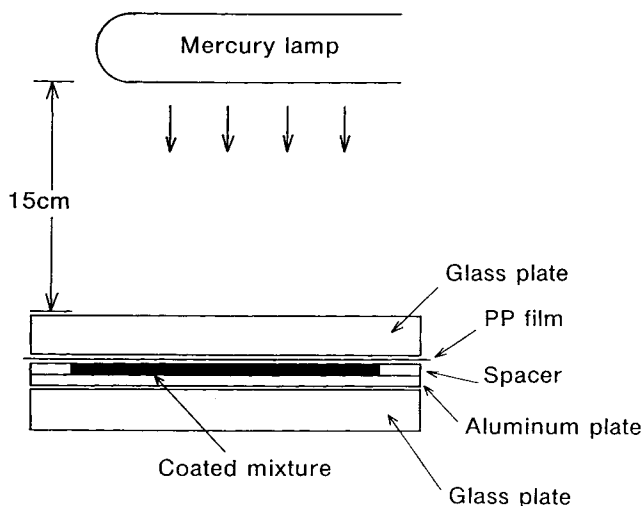[a] Quantities are in parts per hundred resin (phr) by weight.
[b] Bisphenol A type epoxy resin (Epikote 828).
[c] *n*-Butyl acrylate.
[d] Ethyl acrylate.
[e] Benzyl dimethyl ketal (Irgacure 651).
[f] 2,4,6-tris (dimethyl aminomethyl) phenol (DMP-30).

Fig. 1. Schematic view of the preparation conditions for cured epoxy resin modified with acrylic polymer.

The total weight of these materials was about 20 g. The mixture was degassed in a vacuum desiccator at room temperature until frothing stopped. As shown in Figure 1, the mixture was then coated on an aluminum plate (10 × 10 cm, thickness: 0.2 mm) and covered with a polypropylene (PP) film (thickness: 40 μm) and fastened with two glass plates using two clips.

A two-step procedure was employed to prepare the modified epoxy resin. In the first step, *in situ* UV radiation polymerizations for each of the acrylic monomers were carried out at room temperature with a mercury lamp (SHL-100UV type, Toshiba Co.). The polymerization temperature was held at 8–10°C by using an air conditioner. In the second step, the coated aluminum plate fastened with the glass plates was heated at 80°C for 2 h. Then, the glass plates and the PP film were removed and the coated aluminum plate was cut into rectangular specimens with a 15 mm width each. These specimens were heated at 180°C for 4 h.

Internal Stress

When the above specimens were cooled to room temperature, they curled due to the difference between the linear thermal expansion coefficients of the aluminum plate and the cured modified epoxy resin. The internal stress was calculated by a method[15, 16] described in detail in previous articles.[10, 11]

Measurements

Linear thermal expansion coefficients of the cured epoxy resins were measured by thermal mechanical analysis (SSC/560M-type, Seiko Denshi Co.) at a heating rate of approximately 5°C/min for the sample specimen with about a 1.0 mm thickness. This measurement was described in detail in a previous article.[10] Dynamic mechanical properties were measured under tensile condition with Spectrometer (VES-F III type, Iwamoto Co.) at 10 Hz with a heating rate of approximately 2°C/min.

Conditions of Morphology Observations

The surface morphologies of the cured epoxy resins fractured in liquid nitrogen were observed by a scanning electron microscope (SEM, S-450 type, Hitachi Ltd.).

A small piece of the cured epoxy resins was embedded and cured in a fixating epoxy resin (Spurr, Polysciences). The cured blocks were divided into sections with about 800 Å thickness using an ultramicrotome (MT-6000 type, Sorvall Co.). The thin cross sections were mounted on copper grids, stained with a 2% RuO_4 aqueous solution for 20 s, and then dried in a desiccator and observed with a transmission electron microscope (TEM, H-800 type, Hitachi).

RESULTS AND DISCUSSION

The solubility parameter values of PBA,[17] PEA,[17] and the epoxy resin[18] are 8.8, 9.4 and 10.9 $(cal/cm^3)^{1/2}$, respectively. When the PEA and the PBA films (30 × 10 × 0.5 mm) were each dipped in the epoxy resin at 80°C for 48 h, the PEA film dissolved, while the PBA film only swelled slightly and became turbid, although it had no crosslinks. This indicates that the compatibility between the PEA and the epoxy resin was higher than that between the PBA and the epoxy resin. Before the *in situ* polymerization (first step), the epoxy resin–acrylic monomer mixtures were transparent. After the polymerizations at 8–10°C, both mixtures became turbid. The PBA-modified epoxy resin was more turbid than the PEA-modified resin.

SEM micrographs of the fractured cross sections of the unmodified and the modified cured epoxy resins are shown in Figure 2. In the PBA-modified resin (b–d), 0.2–1 μm diameter dispersed domains consisting of the PBA-rich component were clearly observed and their domain/matrix interfaces were well defined. In the PEA-modified resin (e–g), however, the domains were not observed as clearly as those in the PBA-modified resin, except for the 5 phr modified resin.

TEM micrographs of the RuO_4-stained thin sections of the 20 phr modified cured epoxy resins are shown in Figure 3. In the PBA modified resin [Fig. 3(a)], the same type of 0.2–0.5 μm diameter PBA domains were observed by TEM as same as the result observed by SEM [Fig. 2(d)]. In the PEA-modified resin [Fig. 3(b)], however, the morphology was more complex and many 80–200 μm long irregularly shaped clusters were observed. Moreover, in the large clusters [Fig. 3(c)], the 0.5–2.5 μm diameter epoxy domains were dispersed in the PEA-rich matrix, where only the PEA-rich region, not the epoxy domains, was adsorbed with RuO_4. Figure 3(d) shows the morphology of the
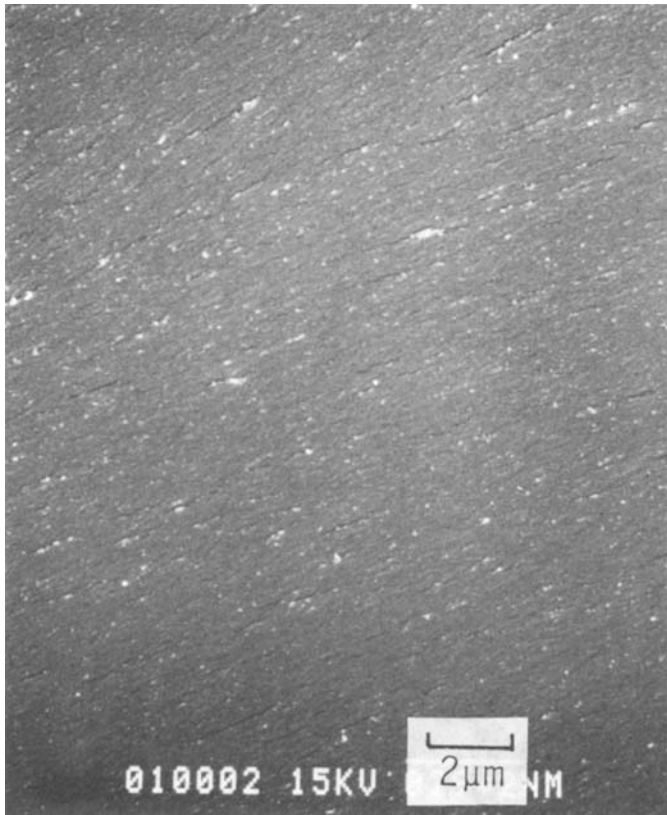
(a)

Fig. 2. SEM micrographs of the fractured cross-sections of unmodified cured epoxy resin and those modified with acrylic polymers produced by *in situ* UV radiation polymerization. (a) Unmodified. (b) Modified with PBA (5 phr). (c) Modified with PBA (10 phr). (d) Modified with PBA (20 phr). (e) Modified with PEA (5 phr). (f) Modified with PEA (10 phr). (g) Modified with PEA (20 phr). (h) Modified with PBA (20 phr): *In situ* polymerized mixture (1st step) was dissolved in toluene and cast before curing (2nd step). (i) Modified with PEA (20 phr): *In situ* polymerized mixture (1st step) was dissolved in toluene and cast before curing (2nd step).

area other than the above-mentioned large clusters. The PEA-rich domains were dispersed in the epoxy matrix. In the domains, the microphase separation was observed.

The dynamic mechanical properties of the unmodified and the 10 phr modified epoxy resins are shown in Figure 4. Each sharp peak of tan δ at 120–140°C is a result of the glass transition temperature (T_g) of the cured epoxy matrix. In the unmodified resin, a broad peak of tan δ at about -80°C was due to the β-relaxation of the cured epoxy matrix. In the PBA- and PEA-modified resins, the broad peaks of tan δ were observed at about -60 and -20°C, respectively. These values corresponded to those of T_g's for PBA and PEA. The tan δ values in the -20–80°C range were ranked in the order of PEA > PBA > the unmodified resin.
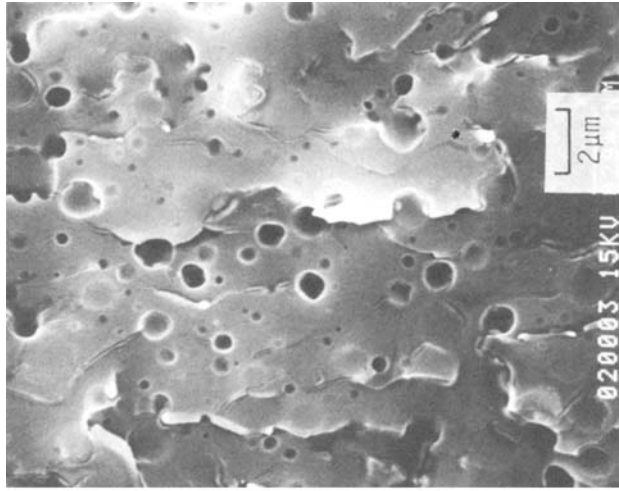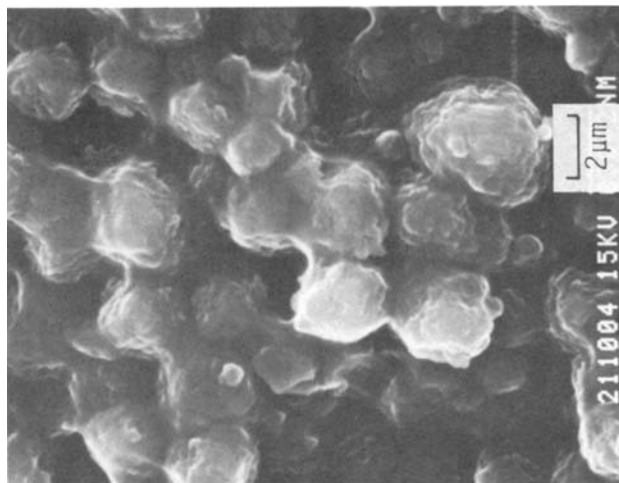
(d)
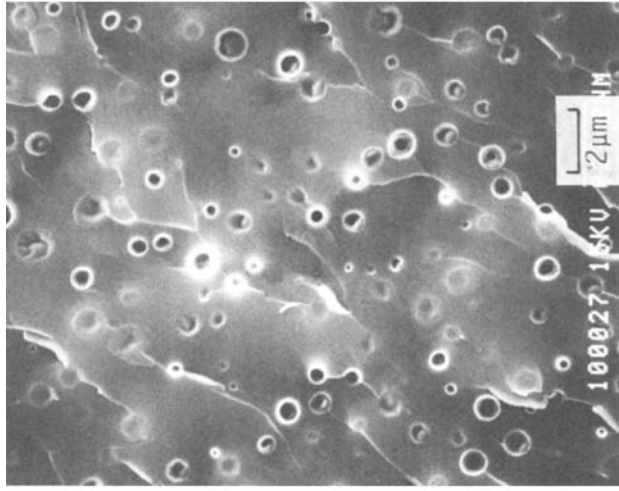
(c)
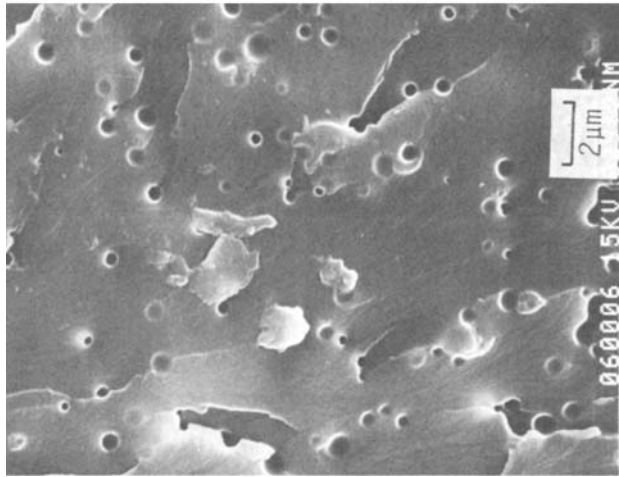
(b)

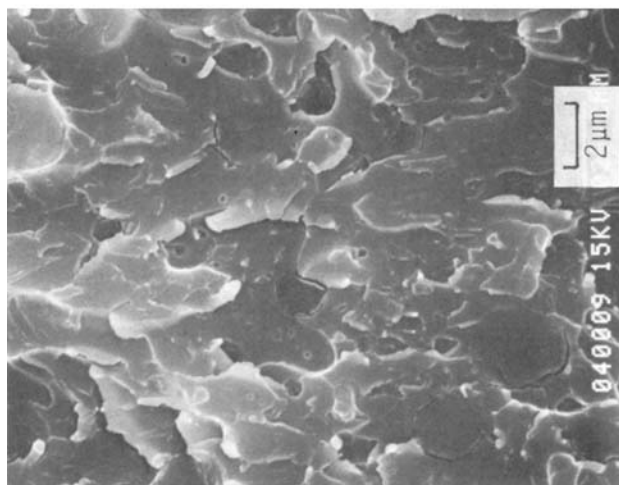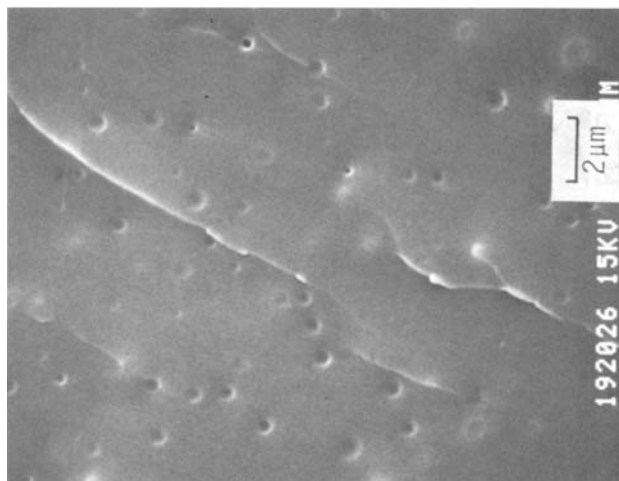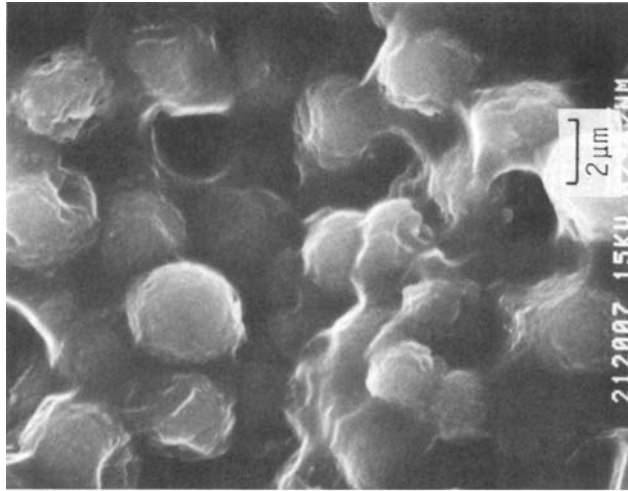Fig. 2. (Continued from the previous page.)
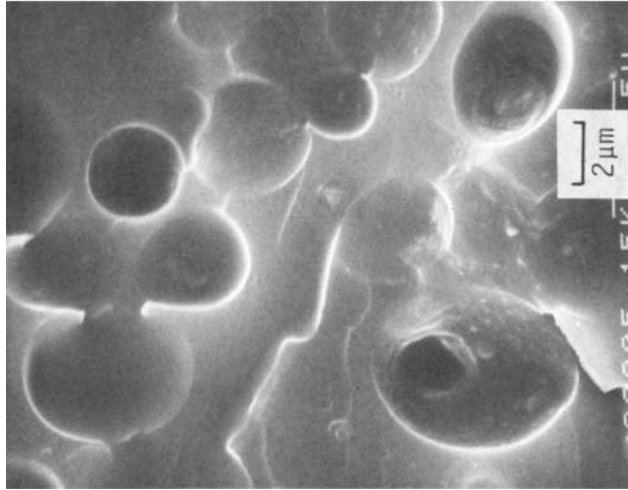
Fig. 2. (Continued from the previous page.)
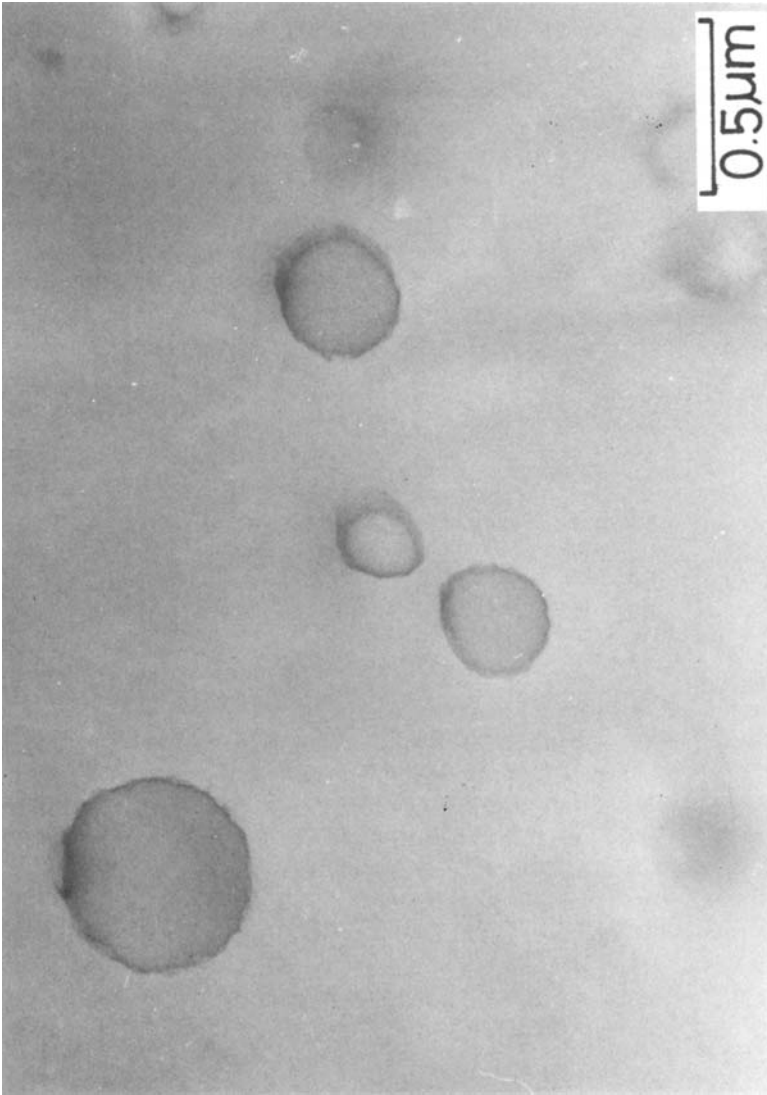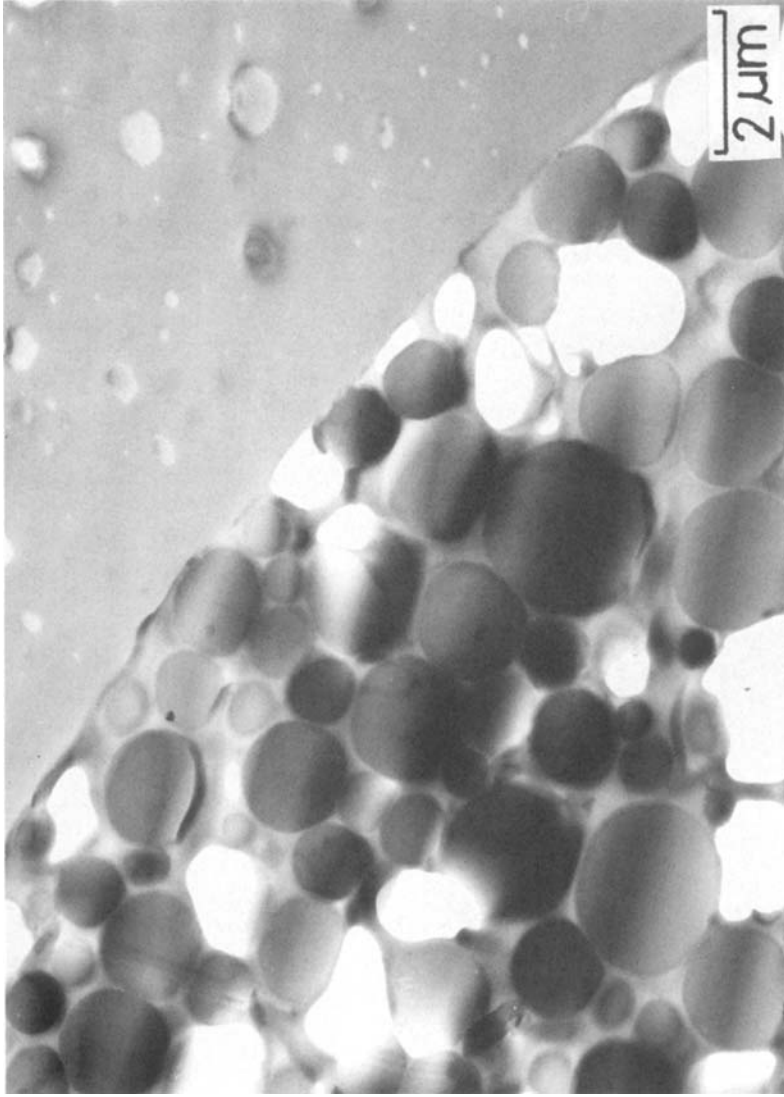
Fig. 2. (Continued from the previous page.)

(a)

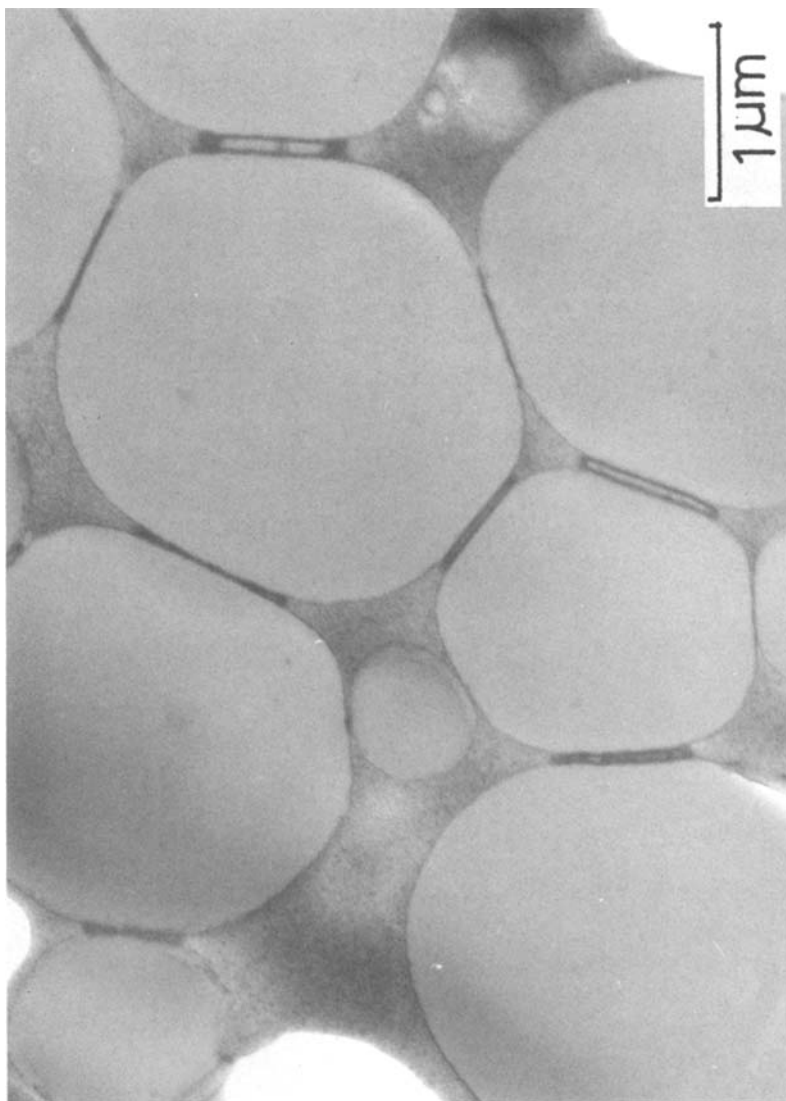Fig. 3. TEM micrographs of RuO$_4$ stained thin sections of 20 phr modified cured epoxy resins. (a) Modified with PBA. (b) Modified with PEA. (c) Modified with PEA. (d) Modified with PEA.
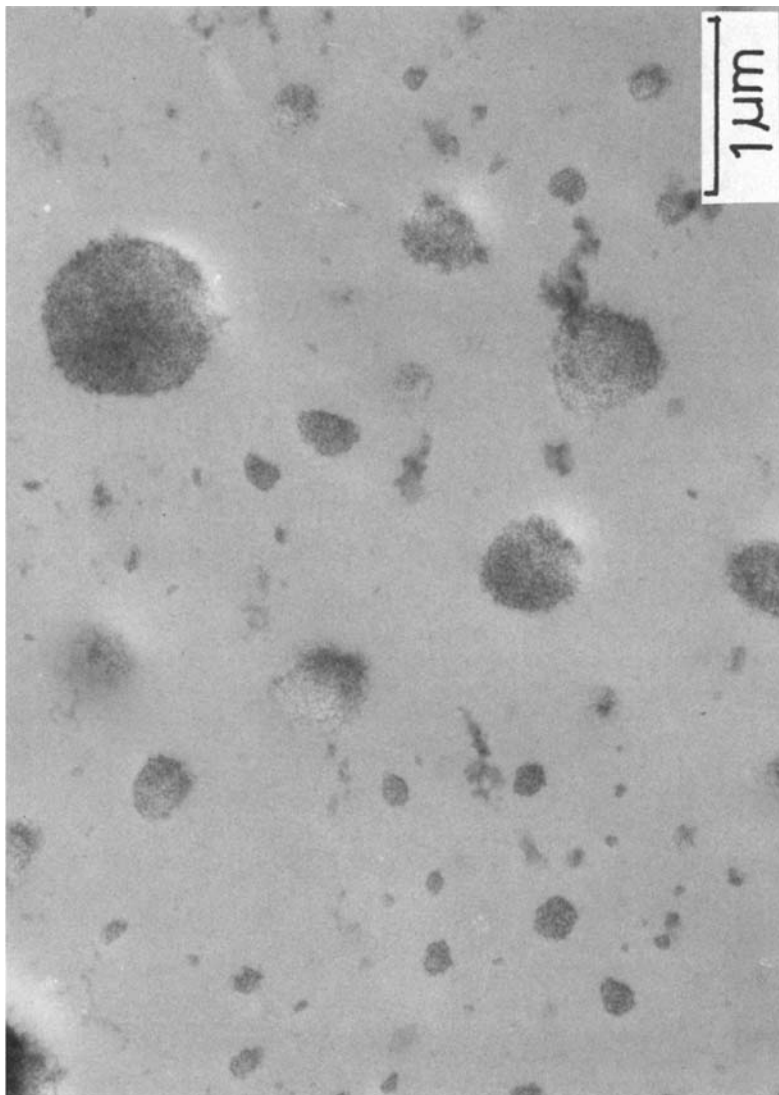
2 μm

(b)

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

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

(c)

1 μm

(d)

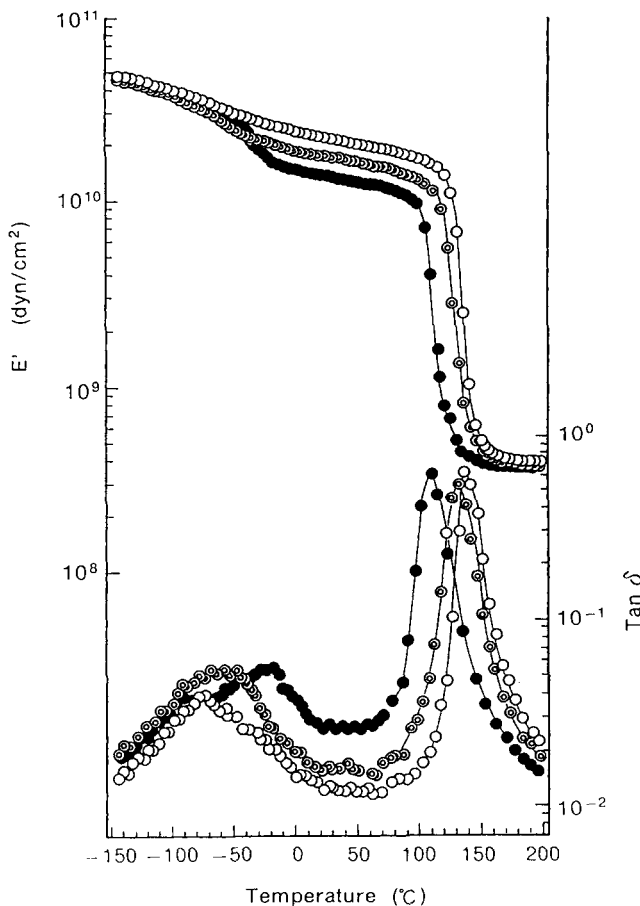Fig. 3. *(Continued from the previous page.)*

Fig. 4. Dynamic mechanical properties of unmodified cured epoxy resin (○) and those modified with PBA (◎) and PEA (●) produced by *in situ* UV radiation polymerization. Acrylic polymer content: 10 phr.

The storage modulus (E') values at 25°C and the T_g value obtained from these dynamic mechanical curves are plotted against the acrylic polymer content in Figure 5. Both the E' and T_g values decreased as a result of the modifications, and they were lower in the PEA modified resin than in the PBA modified resin. The results shown in Figures 2–5 indicate that the miscibility between the acrylic polymer molecules and the epoxy resin was higher in the PEA modified resin than in the PBA modified resin.

The internal stress values are shown in Figure 6. In the PBA-modified resin, the internal stress decreased steadily with an increase in the PBA content. In the PEA-modified resin, however, the internal stress decreased until the PEA content reached 10 phr, but and subsequently increased when PEA increased over 10 phr.

The thermal expansion coefficient (α_1) values below T_g of the cured epoxy resin are shown in Figure 7. In both modified cured epoxy resins, the α_1 values increased with an increase in the acrylic polymer contents. This tendency was more significant in the PEA-modified resin than in the PBA modified resin.
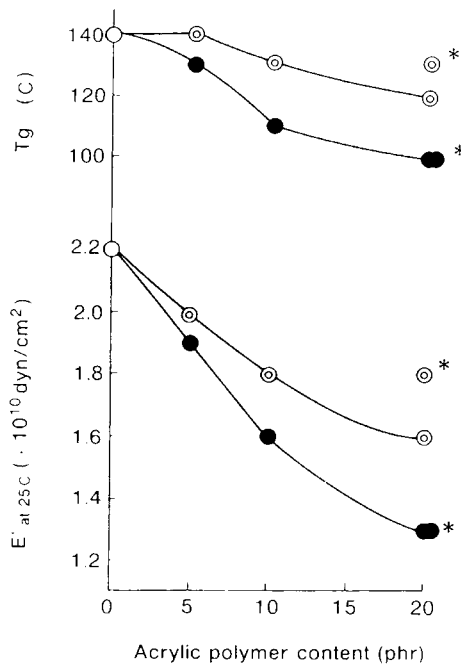
Fig. 5. Storage modulus (E′) at 25°C and T_g of unmodified cured epoxy resin (○) and those modified with PBA (◎) and PEA (●) produced by *in situ* UV radiation polymerization. (∗) *In situ* polymerized mixture (1st step) was dissolved in toluene and cast before curing (2nd step).

The internal stress was calculated by the following equation[1-3]:

$$\sigma = \int_{25°C}^{T_g} E'_{at\,25'C} \cdot (\alpha_1 - \alpha_a)\, dt \qquad (1)$$

where σ is the internal stress, α_a is the thermal expansion coefficient of the aluminum plate $(2.6 \times 10^{-5}/°C)$,[19] and E', T_g, and α_1 are defined as above.

The internal stress values calculated from eq. (1) using the values obtained in Figures 5 and 7 are shown in Figure 8. In both modified cured epoxy resins, the calculated internal stress decreased with an increase in their acrylic
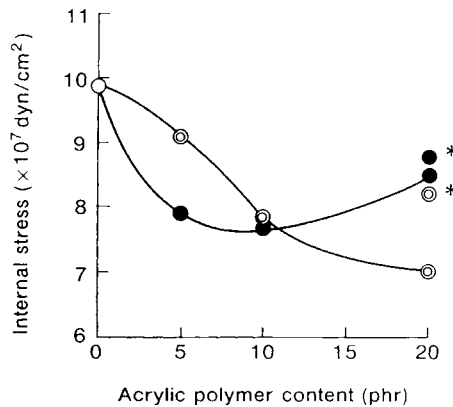

Fig. 6. Internal stress of unmodified cured epoxy resin (○) and those modified with PBA (◎) and PEA (●) produced by *in situ* UV radiation polymerization. (∗) *In situ* polymerized mixture (1st step) was dissolved in toluene and cast before curing (2nd step).

Fig. 7. Thermal expansion coefficient (α_1) below T_g of unmodified cured epoxy resin (○) and those modified with PBA (◎) and PEA (●) produced by *in situ* UV radiation polymerization. (*) *In situ* polymerized mixture (1st step) was dissolved in toluene and cast before curing (2nd step).
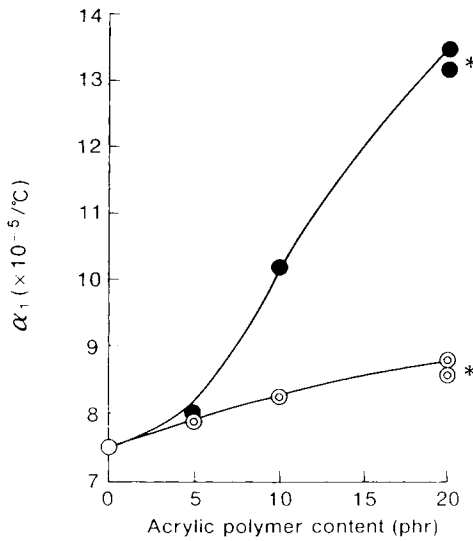
polymer contents. This tendency corresponds to the experimental results shown in Figure 4, although the absolute values of the calculated results were somewhat larger than those of the experimental results.

In Figures 5–8, the asterisked (*) data indicate the results of the cured films cast from a toluene solution in which the epoxy resins modified by the *in situ*
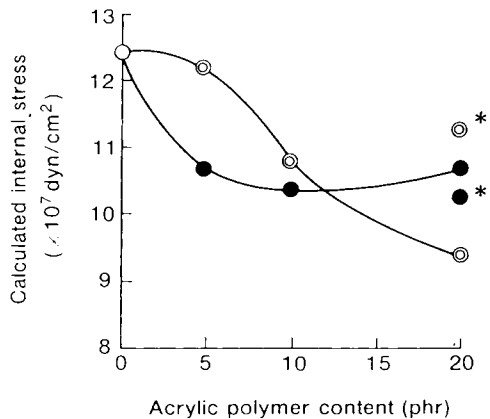

Fig. 8. Calculated internal stress of unmodified cured epoxy resin (○) and those modified with PBA (◎) and PEA (●) produced by *in situ* UV radiation polymerization. (*) *In situ* polymerized mixture (1st step) was dissolved in toluene and cast before curing (2nd step). Calculated by

$$\sigma = \int_{25°C}^{T_g} E'_{\text{at } 25°C} \cdot (\alpha_1 - \alpha_a) \, dt$$

where σ is the internal stress, E' is the storage modulus of cured epoxy resin, T_g means the T_g of cured epoxy resin, α_1 is the thermal expansion coefficient of cured epoxy resin below T_g, and α_a is the thermal expansion coefficient of an aluminum plate.

UV radiation polymerization for BA and EA were dissolved. In the PEA-modified resin, the E' and the T_g (Fig. 5), the internal stress (Fig. 6), and the α_1 values (Fig. 7) were the same as those of the undissolved original type. In the PBA-modified resin, the E' and the T_g (Fig. 5) and the internal stress (Fig. 6) values were larger than those of the undissolved original type, while the α_1 values (Fig. 7) were the same. In the PEA-modified resin [Fig. 2(i)], the morphology was almost the same as that of the undissolved original film [Fig. 2(g)]. In the PBA-modified resin [Fig. 2(h)], however, the domain size of the cast film was much larger than that of the unmodified original film [Fig. 2(d)]. These phenomena closely correspond to the results in a previous article[10] that showed the decrease of the E' due to a decrease in the domain size effectively reduced the internal stress.

CONCLUSION

It was concluded that the PBA modified resin, having low compatibility, was more suitable than the PEA modified resin with high compatibility. This conclusion is based on PBA's advantage reducing the internal stress without lowering the heat resistance of epoxy resin.

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