Internal stress of epoxy resin modified with acrylic polymers having crosslinks produced by *in situ* UV radiation polymerization

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In order to reduce the internal stress of cured epoxy resin generated by shrinkage in the cooling process from cure temperature to room temperature, two kinds of acrylic polymers were introduced by *in situ* UV radiation polymerization prior to curing. Polybutyl acrylate (A) and butyl acrylate-monoethylene glycol dimethacrylate copolymer (molar ratio 95 : 5) (B) were used as the acrylic polymer. In the A-modified resin, a heterogeneous structure with spherical submicrometre domains were formed. In the B-modified resin, irregularly shaped submicrometre domains in which the microphase separation occurred were observed. The modulus of cured epoxy resin decreased as a result of the modifications, and was lower in the B-modified resin than in the A-modified resin. Therefore the internal stress decreased more effectively in the B-modified resin.

1. 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 process of cooling to room temperature [1-3]. This internal stress reduces adhesive strength and occasionally causes cracks in the casting material [4-6].

Previous research has 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 this research, the modified epoxy resins had heterogeneous structures with the elastomer dispersed as domains in the epoxy matrix.

In our previous articles [10, 11], the effect of heterogeneous structure on internal stress has been studied using polybutyl acrylate (PBA)/polymethyl methacrylate core-shell particles. As a result, it was shown that the internal stress was effectively reduced by decreasing the domain size which corresponded to the PBA core size [10], and further by introducing a strong interaction at the domain/matrix interface [11].

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

resin by introducing the uncrosslinked polymers using similar procedures [15].

In this article the *in situ* UV radiation copolymerization for *n*-butyl acrylate (BA) and monoethylene glycol dimethacrylate (1G) was carried out to examine the effect of crosslinks in the modifier on internal stress.

2. Experimental procedure
2.1. 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 in curing the epoxy resin. BA and ethyl acrylate (EA) were purified by distillation at reduced pressure in a nitrogen atmosphere and then stored in a refrigerator. Commercial grade 1G and benzyl dimethyl ketal (Irgacure 651, Ciba-Geigy Ltd) were used as crosslinking agent and UV-sensitive initiator, respectively.

2.2. *In situ* UV radiation polymerization

Table I shows the formulations of the modified epoxy resins. BA (or BA + 1G, 95 : 5 molar ratio) monomer, the UV-sensitive initiator and the accelerator were added to the epoxy resin and hand-mixed using a spatula for 5 min at room temperature. 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 described in detail in our previous report [15], the mixture was then coated on an aluminium plate (10 × 10 cm, 0.2 mm
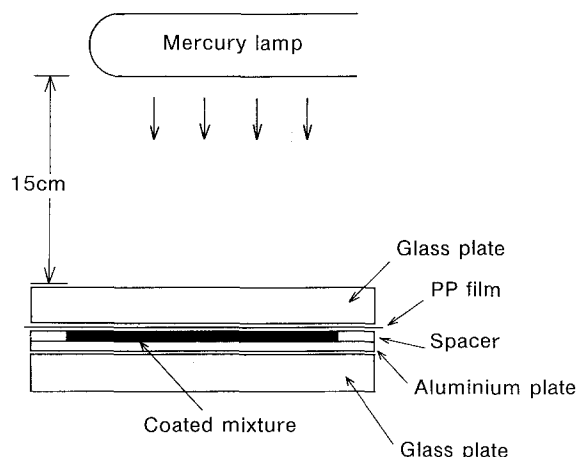
Figure 1 Schematic view of the preparation conditions for cured epoxy resin modified with acrylic polymer. 1st step: *in situ* UV radiation polymerization of acrylic monomer (8 to 10°C, 4h). 2nd step: curing of epoxy matrix (80°C, 2 h + 180°C, 4 h).

thick) and covered with a polypropylene (PP) film (40 μm thick) and fastened with two glass plates using two clips (see Fig. 1).

A two-step procedure was employed to prepare the modified epoxy resin. In the first step, the *in situ* UV radiation polymerization was carried out in the fastened mixture with a mercury lamp (SHL-100UV, Toshiba Co.). The polymerization temperature was held at 8 to 10°C using an air conditioner. In the second step, the coated aluminium 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 aluminium plate was cut into rectangular specimens of 15 mm wide. These specimens were heated at 180°C for 4 h.

2.3. 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 aluminium plate and the cured modified epoxy resin. The internal stress was measured by a procedure [16, 17] described in detail in a previous article [10].

2.4. Measurements

Linear thermal expansion coefficients of the cured epoxy resins, dynamic mechanical properties and morphologies of the unmodified and modified cured epoxy resins were measured as described in our previous articles [10, 11].

3. Results and discussion

Before the *in situ* polymerization (1st step), the epoxy resin–acrylic monomer (BA or BA + 1G (95 : 5 molar ratio)) mixtures were transparent. After polymerization, both mixtures became turbid. When the polymerized mixtures were dipped in toluene, the mixture with PBA dissolved completely, whereas the mixture with BA-1G copolymer (P(BA-1G)) remained undissolved in part. That is, in the latter case a network of acrylic polymer formed in the epoxy matrix. Therefore after curing of the epoxy matrix (2nd step), IPN [14] should be formed between the cured epoxy resin and P(BA-1G). The results for the mixtures with EA monomer and with EA + 1G monomers were obtained to compare with the above results, and will be discussed below.

Fig. 2 shows SEM micrographs of the fractured cross-sections of the 5 to 20 parts per hundred resin (p.h.r.) modified cured epoxy resins. In the PBA-modified resins (a–c), dispersed domains ranging from 0.2 to 1 μm in diameter were clearly observed. In the P(BA-1G)-modified resins (d–f), the formation of domains was not clear and the fractured surfaces were rough and irregular.

Fig. 3 shows TEM micrographs of the RuO_4-stained thin sections of 10-p.h.r.-modified cured epoxy resins. In the PBA-modified resin (Fig. 3a), PBA domains about 0.2 μm in diameter were observed, in accord with SEM observations (Fig. 2b). In the P(BA-1G)-modified resin (Fig. 3b), however, irregularly shaped domains were observed. Moreover, in

TABLE I Formulations of modified epoxy resins*

Sample No.	1	2	3	4	5	6	7	8	9
	Unmodified	Modified							
Acrylic polymer	–	PBA	PBA	PBA	P(BA–1G)	P(BA–1G)	P(BA–1G)	PEA	P(EA–1G)
Acrylic polymer content (p.h.r.)	0	5	10	20	5	10	20	10	10
Epoxy resin[†]	100	100	100	100	100	100	100	100	100
BA monomer[‡]	–	5	10	20	4.63	9.25	18.49	–	–
EA monomer[§]	–	–	–	–	–	–	–	10	9.06
1G monomer[•]	–	–	–	–	0.37	0.75	1.51	–	0.94
UV-sensitive initiator[**]	–	0.03	0.06	0.12	0.03	0.06	0.12	0.06	0.06
Accelerator[‡‡]	4	4	4	4	4	4	4	4	4

*Quantities are in parts per hundred resin (p.h.r.) by weight.
[†] Bisphenol A-type epoxy resin (Epikote 828).
[‡] n-Butyl acrylate.
[§] Ethyl acrylate.
[•] Monoethylene glycol dimethacrylate.
[**] Benzyl dimethyl ketal (Irgacure 651).
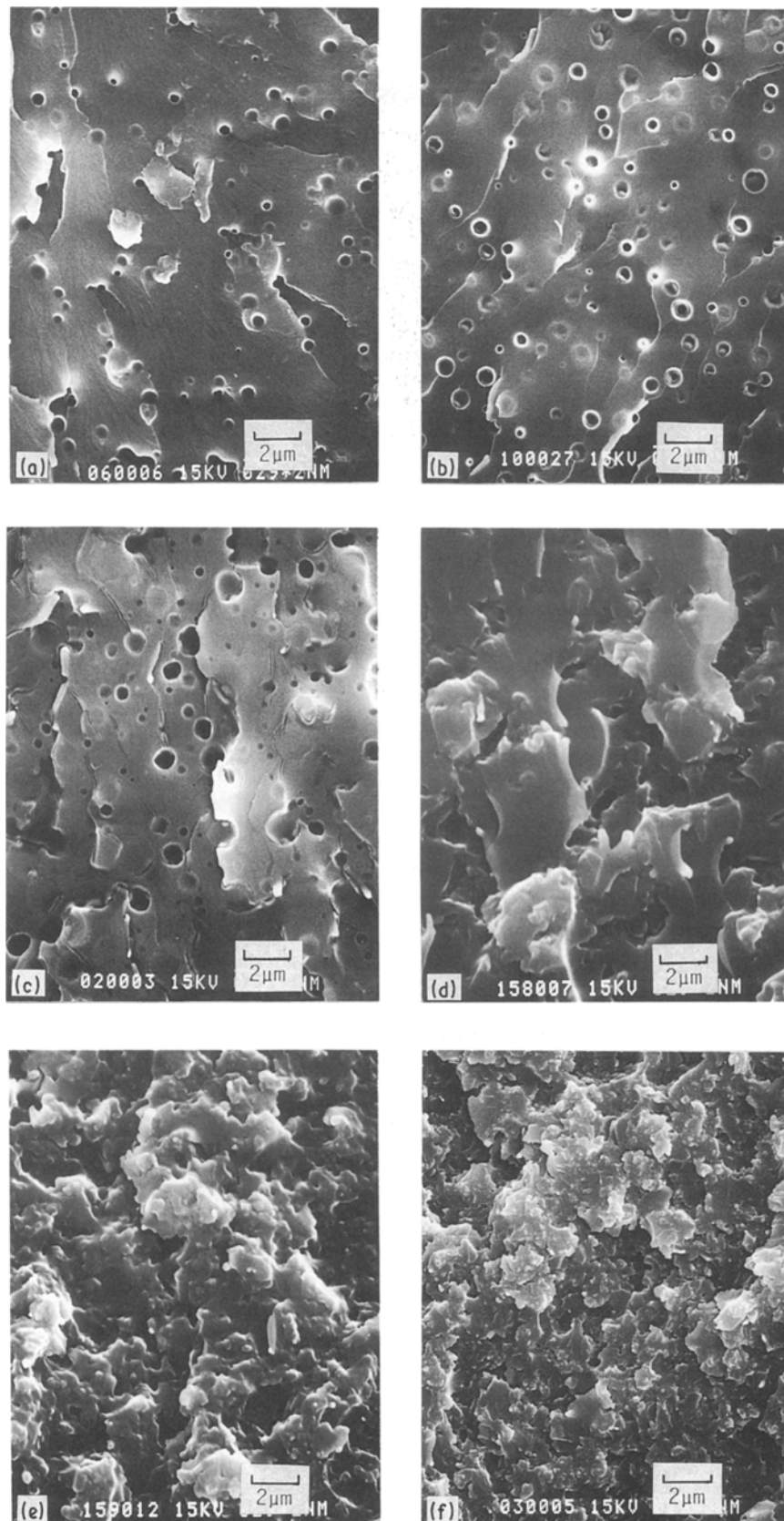[‡‡] 2,4,6-tris (dimethyl aminomethyl) phenol (DMP-30).

Figure 2 SEM micrographs of the fractured cross-sections of cured epoxy resins modified with acrylic polymers produced by *in situ* UV radiation polymerization. Modified with (a) PBA, 5 p.h.r.; (b) PBA, 10 p.h.r.; (c) PBA, 20 p.h.r.; (d) P(BA–1G), 5 p.h.r.; (e) P(BA–1G), 10 p.h.r.; (f) P(BA–1G), 20 p.h.r.; (g) PEA, 10 p.h.r.; (h) P(EA–1G), 10 p.h.r..

the domain a micro phase separation structure was observed.

Fig. 4 shows the dynamic mechanical properties of the unmodified and modified epoxy resins with 10 p.h.r. PBA and P(BA–1G). Each sharp peak of tan δ at 120 to 140° C was due to 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-modified resin, the broader peak of tan δ was observed around $-60°$ C which corresponded to the T_g for PBA. In the P(BA–1G)-modified
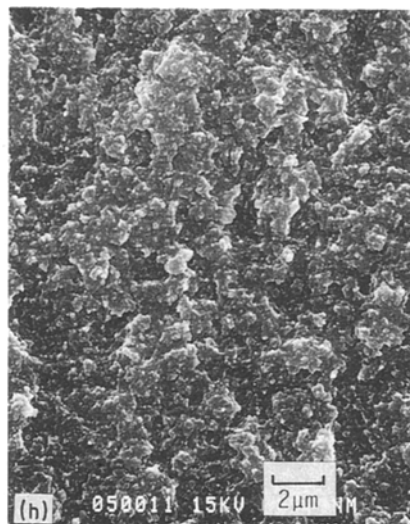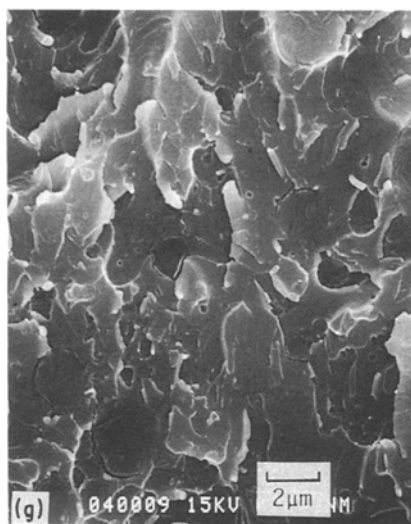
resin, the tan δ peak at the low temperature region was broadest. The tan δ values in the range of -20 to $80°$ C were ranked in the order P(BA–1G) > PBA > unmodified resin.

Fig. 5 shows the relationships between the acrylic polymer content and the storage modulus (E') values at $25°$ C and the T_g values of the cured epoxy matrix obtained from the above dynamic mechanical curves. Both E' and T_g values decreased as a result of the modification, and were lower in the P(BA–1G)-modified resin than in the PBA-modified resin. The results shown in Figs 2–5 indicate that the apparent miscibility between the acrylic polymer molecules and the epoxy resin was higher in the P(BA–1G)-modified

resin than in the PBA-modified resin. This seems to be derived from the fact that the phase separation was depressed by the crosslinks already formed in the *in situ* polymerization process.

Fig. 6 shows the internal stress value. In the PBA- and P(BA–1G)-modified resins, the internal stress decreased with increasing acrylic polymer content, and was lower in the P(BA–1G)-modified resin than in the PBA-modified resin.

Fig. 7 shows the thermal expansion coefficient (α_l) values below T_g of the cured epoxy resin. In the PBA- and the P(BA–1G)-modified resins, the α_l values increased with the increase in acrylic polymer content, and the increase was at almost the same level in both modified resins.

As described in our previous article [15] and by others [1–3], the internal stress was calculated by the following equation

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

where σ is the internal stress, α_a is the thermal expansion coefficient of the aluminium plate and E', T_g and α_l are defined above. It is clear from the results in
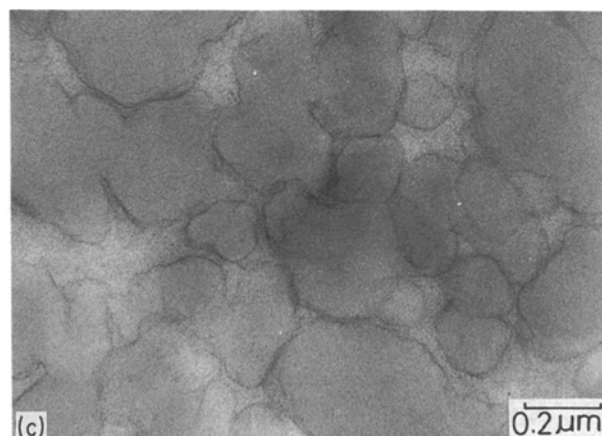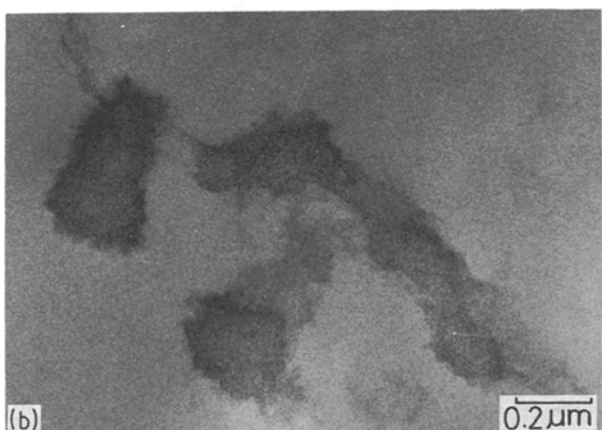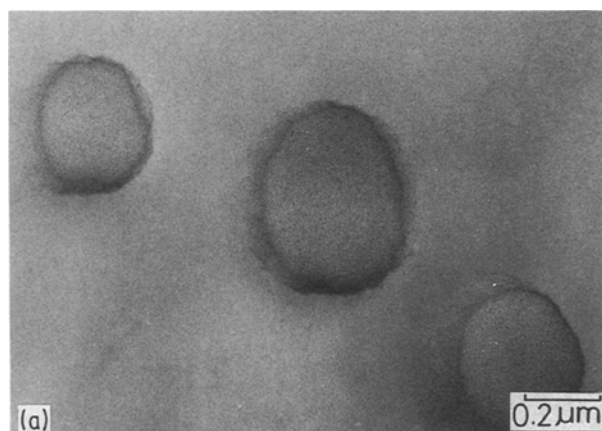

Figure 3 TEM micrographs of RuO_4-stained thin sections of 10-p.h.r.-modified cured epoxy resins. Modified with (a) PBA; (b) P(BA–1G) (95:5, molar ratio); (c) P(EA–1G) (95:5, molar ratio).
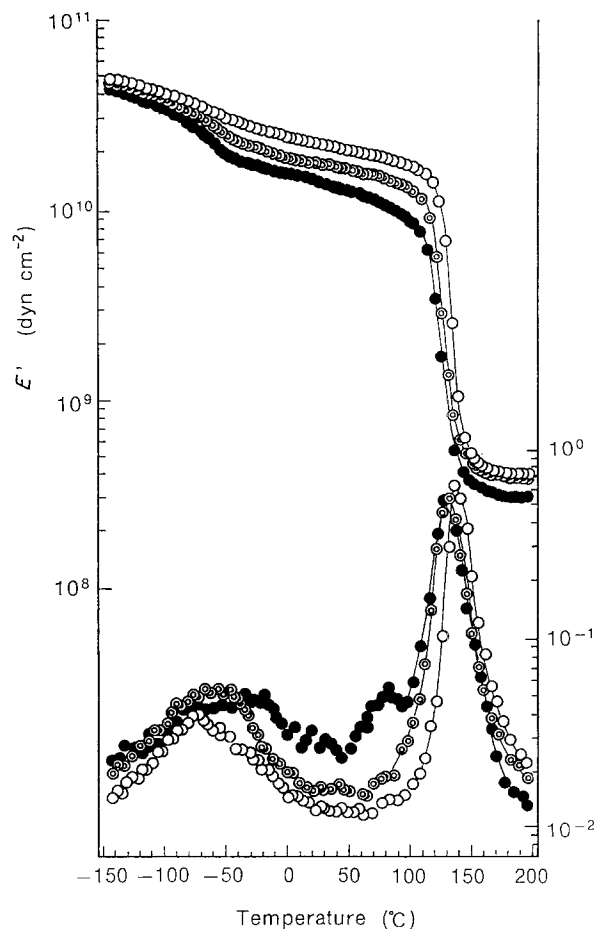
Figure 4 Dynamic mechanical properties of (○) unmodified cured epoxy resin and those (◉) modified with PBA and (●) P(BA–1G) (95:5, molar ratio) produced by *in situ* UV radiation polymerization. Acrylic polymer content: 10 p.h.r.
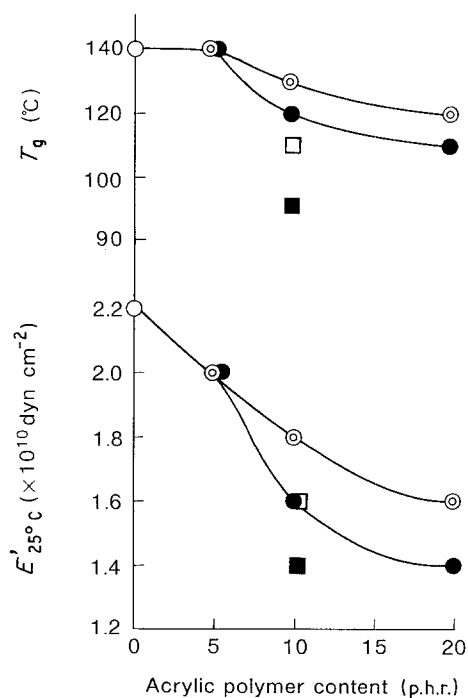

Figure 5 Storage modulus (E′) at 25°C and T_g of (○) unmodified cured epoxy resin and those modified with (◉) PBA, (□) PEA, (●) P(BA–1G) (95:5, molar ratio) and (■) P(EA–1G) (95:5, molar ratio) produced by *in situ* UV radiation polymerization.
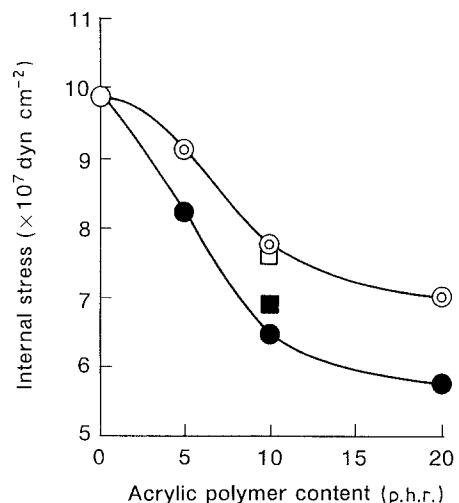

Figure 6 Internal stress of (○) unmodified cured epoxy resin and those modified with (◉) PBA, (□) PEA, (●) P(BA–1G) (95:5, molar ratio) and (■) P(EA–1G) (95:5, molar ratio) produced by *in situ* UV radiation polymerization.

Figs 5–7 and Equation 1 that the decrease of E′ and T_g reduced the internal stress more in the P(BA–1G)-modified resin than in the PBA-modified resin.

The results for PEA and EA–1G copolymer (P(EA–1G), 95:5 molar ratio)-modified (10 p.h.r.) resins are also shown in Figs 2–7. In our previous article [15], it was pointed that the compatibility with the epoxy resin was higher in PEA than in PBA. This is also supported here by the SEM observations (Figs 2b and g) that phase separation in the PEA modified resin is not so clear as that in the PBA-modified resin, and that the E′ and T_g values are lower in the PEA-modified resin (Fig. 5). The α_1 value was, however, higher in the PEA-modified resin than in the PBA-modified resin (Fig. 7). As a result, the internal stress was almost the same in the PEA- and PBA-modified resins (Fig. 6).
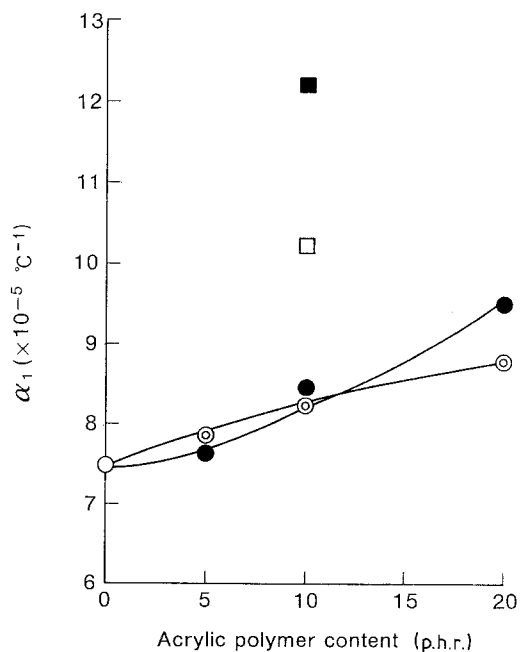

Figure 7 Thermal expansion coefficient (α_1) below T_g of (○) unmodified cured epoxy resin and those modified with (◉) PBA, (□) PEA, (●) P(BA–1G) (95:5, molar ratio) and (■) P(EA–1G) (95:5, molar ratio) produced by *in situ* UV radiation polymerization.

In comparing the morphologies of P(BA–1G)-, PEA- and P(EA–1G)-modified resins by SEM observation (Figs 2e, g and h) and by TEM observation (Figs 3b and c), it is clear that the compatibility between the acrylic polymers and the epoxy resin was higher in the P(EA–1G)-modified resin than in both PEA- and P(BA–1G)-modified resins. The decreases of E' and T_g (Fig. 5) and the increase of α_1 (Fig. 7) were remarkable more in the P(EA–1G)-modified resin than in both PEA- and P(BA–1G)-modified resins, although the internal stress value was nearly at the same level in the P(BA–1G)- and P(EA–1G)-modified resins (Fig. 6).

From the above results, it was concluded that the introduction of PBA with crosslinks to the epoxy resin prior to curing is useful in reducing the internal stress, although the T_g, for example, the heat resistance of the epoxy resin, decreased slightly.

Acknowledgement

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