

Internal stress of epoxy resin modified with acrylic polymers containing functional groups produced by *in situ* u.v. radiation polymerization

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To reduce the internal stress generated in cured epoxy resin by shrinkage in the cooling process from cure temperature to room temperature, three kinds of acrylic polymer were introduced by *in situ* ultraviolet radiation polymerization before the curing. They were polybutyl acrylate (A), butyl acrylate-glycidyl methacrylate copolymer (95/5, mole ratio) (B) and butyl acrylate-monoethylene glycol dimethacrylate copolymer (95/5, mole ratio) (C). In the A and B modified resins, a heterogeneous structure with spherical shaped submicrometre domains consisting of acrylic polymers was formed. In the C modified resin, a heterogeneous structure with irregularly shaped submicrometre domains was formed. Further, in the B and C modified resins, microphase separation was observed in the domains. These results suggest that the interaction between acrylic polymer domains and the epoxy matrix increased in the order C > B > A modified resin. As a result of the modifications, the modulus and the internal stress of cured epoxy resin decreased effectively in the same order.

(Keywords: epoxy resin; acrylic polymer; *in situ* polymerization; internal stress; phase separation; interpenetrating polymer networks (IPN))

INTRODUCTION

Epoxy resin is widely used for coatings, adhesives, casting, electrical insulation and other applications. It is generally acknowledged that an internal stress is generated in cured epoxy resin due to shrinkage in the cooling process from cure temperature to room temperature¹⁻³. This internal stress reduces adhesive strength and occasionally causes cracks in the casting material⁴⁻⁶.

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 copolymer⁷⁻⁹. In this research, the modified epoxy resins had heterogeneous structures, with the elastomer dispersed as domains in the epoxy matrix.

In our previous papers^{10,11}, the effect of heterogeneous structure on internal stress was studied by using polybutyl acrylate (PBA)/polymethyl methacrylate core-shell particles. It was clarified that the internal stress was effectively reduced by decreasing the domain size which corresponded to the PBA core size¹⁰, and further by introducing a strong interaction at the domain/matrix interface¹¹.

Sperling and co-workers prepared materials consisting of epoxy resin and PBA¹² (or polyethyl acrylate¹³) by heat curing and *in situ* ultraviolet (u.v.) radiation polymerization, respectively. They treated them as interpenetrating polymer networks (IPN)¹⁴ and measured the

mechanical properties, but did not refer to the internal stress. Using similar procedures, therefore, we examined the reduction of internal stress on introducing the uncrosslinked polymers¹⁵.

In this study, *in situ* u.v. radiation copolymerization of n-butyl acrylate (BA) with glycidyl methacrylate (GMA) or monoethylene glycol dimethacrylate (1G) was done to examine the effect of the interaction between the acrylic polymer domain and the epoxy matrix due to a chemical reaction or IPN on the reduction of the internal stress.

EXPERIMENTAL

Materials

Bisphenol A type epoxy resin (Epikote 828, Shell Chemical Co.; equivalent weight per epoxy group, 190 ± 5 ; average molecular weight, 380) was used. 2,4,6-Tris(dimethyl aminomethyl) phenol (DMP-30) was used as an accelerator for curing of the epoxy resin. BA was purified by distillation at reduced pressure in a nitrogen atmosphere and then stored in a refrigerator. GMA and 1G were used without further purification. Commercial grade benzyl dimethyl ketal (Irgacure 651, Ciba-Geigy Ltd) was used as a u.v. sensitive initiator.

Sample preparation

Table 1 shows the formulations of the modified epoxy resins. BA monomer (BA + GMA or BA + 1G monomers,

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Table 1 Formulations of modified epoxy resins

Sample no.	1	2	3	4	5	6	7	8	9	10
	Unmodified			Modified						
Acrylic polymer	–	PBA	PBA	PBA	P(BA–GMA)	P(BA–GMA)	P(BA–GMA)	P(BA–1G)	P(BA–1G)	P(BA–1G)
Acrylic polymer content (wt%)	0	5	10	20	5	10	20	5	10	20
Epoxy resin ^a	100	100	100	100	100	100	100	100	100	100
BA ^b monomer	–	5	10	20	4.72	9.45	18.90	4.63	9.25	18.49
GMA ^c monomer	–	–	–	–	0.28	0.55	1.10	–	–	–
1G ^d monomer	–	–	–	–	–	–	–	0.37	0.75	1.51
U.v. sensitive initiator ^e	–	0.03	0.06	0.12	0.03	0.06	0.12	0.03	0.06	0.12
Accelerator ^f	4	4	4	4	4	4	4	4	4	4

^a Bisphenol A type epoxy resin (Epikote 828)^b n-Butyl acrylate^c Glycidyl methacrylate^d Monoethylene glycol dimethacrylate^e Benzyl dimethyl ketal (Irgacure 651)^f 2,4,6-Tris (dimethyl aminomethyl) phenol (DMP-30)

95/5 mole ratio), the u.v. sensitive initiator and the accelerator were added to the epoxy resin and hand-mixed using a spatula at room temperature for 5 min. The total weight of these materials was ≈ 20 g. The mixture was degassed in a vacuum desiccator at room temperature until frothing stopped. As described in detail previously¹⁵, the mixture was then coated on an aluminium plate (10×10 cm²; thickness, 0.2 mm), covered with a polypropylene (PP) film (thickness 40 μ m) and fastened with two glass plates using two clips (see Figure 1).

A two-step procedure was used to prepare the modified epoxy resin. First, *in situ* u.v. radiation polymerization was carried out in the fastened mixture with a mercury lamp (SHL-100UV, Toshiba Co.). The polymerization temperature was held at 8–10°C using an air conditioner. Second, 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, each of width 15 mm. 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 aluminium plate and the cured modified epoxy resin. The internal stress was measured by a procedure^{16,17} described in detail previously¹⁰.

Measurements

Linear thermal expansion coefficients of the cured epoxy resins and morphologies of the modified cured epoxy resins were measured by methods described previously^{10,11}. Dynamic mechanical properties were measured under tensile conditions with a dynamic viscoelastometer (Rheovibron DDV-III-EP type, Orientec Corp.) at 11 Hz with a heating rate of $\approx 2^\circ\text{C min}^{-1}$.

RESULTS AND DISCUSSION

Before the *in situ* polymerization (first step), the epoxy resin–acrylic monomer (BA, BA + GMA, or BA + 1G) mixtures were transparent. After polymerization, the three types of mixture became turbid. When the polym-

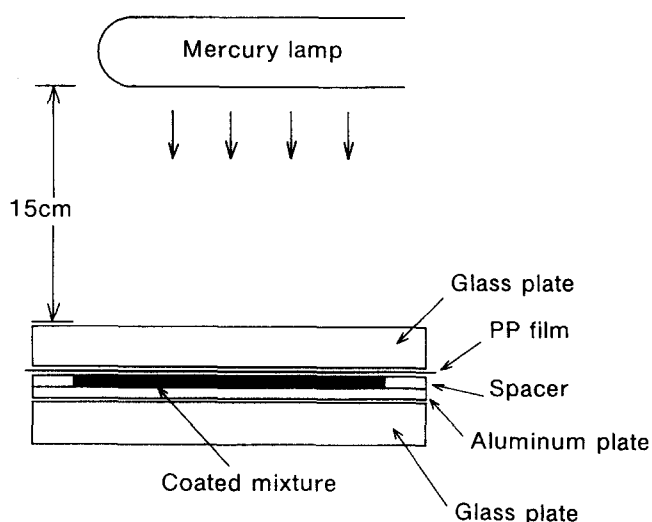


Figure 1 Schematic view of the preparation conditions for cured epoxy resin modified with acrylic polymer

erized mixtures were dipped in toluene, the mixture containing PBA or BA–GMA copolymer (P(BA–GMA)) dissolved completely, whereas the mixture containing BA–1G copolymer (P(BA–1G)) did not dissolve partially. This suggests that in the latter case a network of acrylic polymer is formed in the epoxy matrix. Therefore, after curing of the epoxy matrix (second step), IPN¹⁴ should be formed between the cured epoxy resin and P(BA–1G). In the P(BA–GMA) modified resin, epoxy groups in acrylic polymer should react with the epoxy matrix in the second step (curing process).

Figure 2 shows SEM micrographs of the fractured cross sections of the 20 wt% modified cured epoxy resins. Both in the PBA and in the P(BA–GMA) modified resins (Figures 2a and b), the spherical shaped domains ranging from 0.2 to 2 μ m in diameter are clearly observed as holes. In the former, polymer particles had fallen away; in the latter they still remained in the holes. In contrast, in the P(BA–1G) modified resin (Figure 2c), domain formation is not clear and the fractured surface is rough and irregular.

Figure 3 shows TEM micrographs of RuO₄-stained thin sections of 20 wt% modified cured epoxy resins. In the PBA and P(BA–GMA) modified resins (Figures 3a and b), spherical shaped domains are observed,

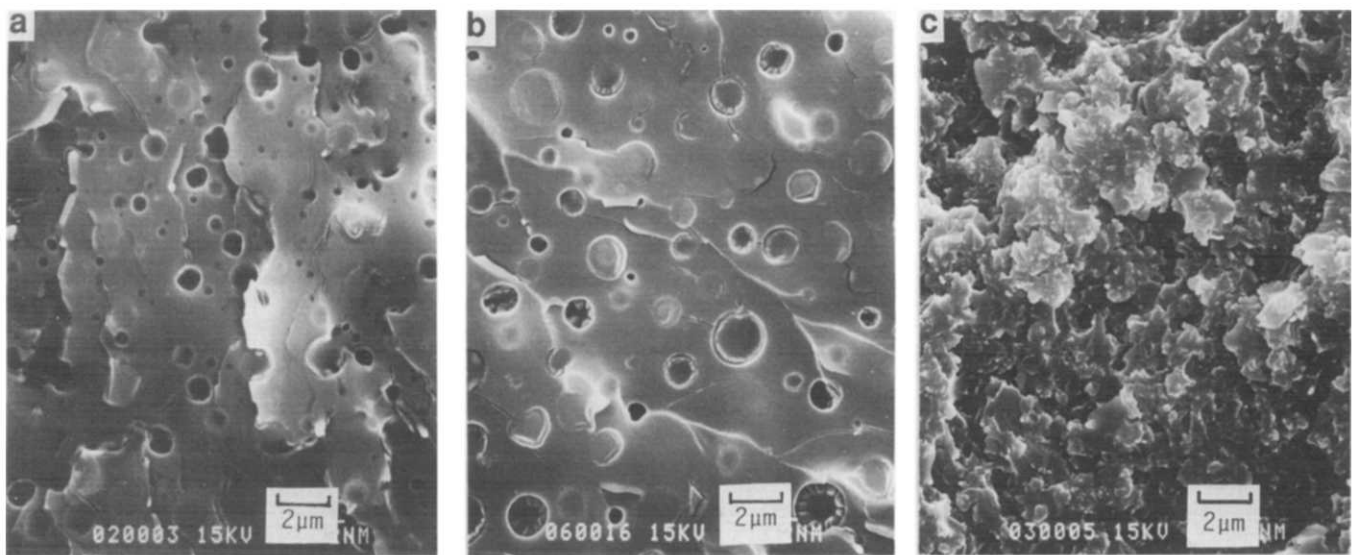


Figure 2 SEM micrographs of the fractured cross-sections of cured epoxy resins 20 wt% modified with acrylic polymers produced by *in situ* u.v. radiation polymerization: (a) modified with PBA; (b) P(BA-GMA) (95/5 mole ratio); (c) P(BA-1G) (95/5 mole ratio)

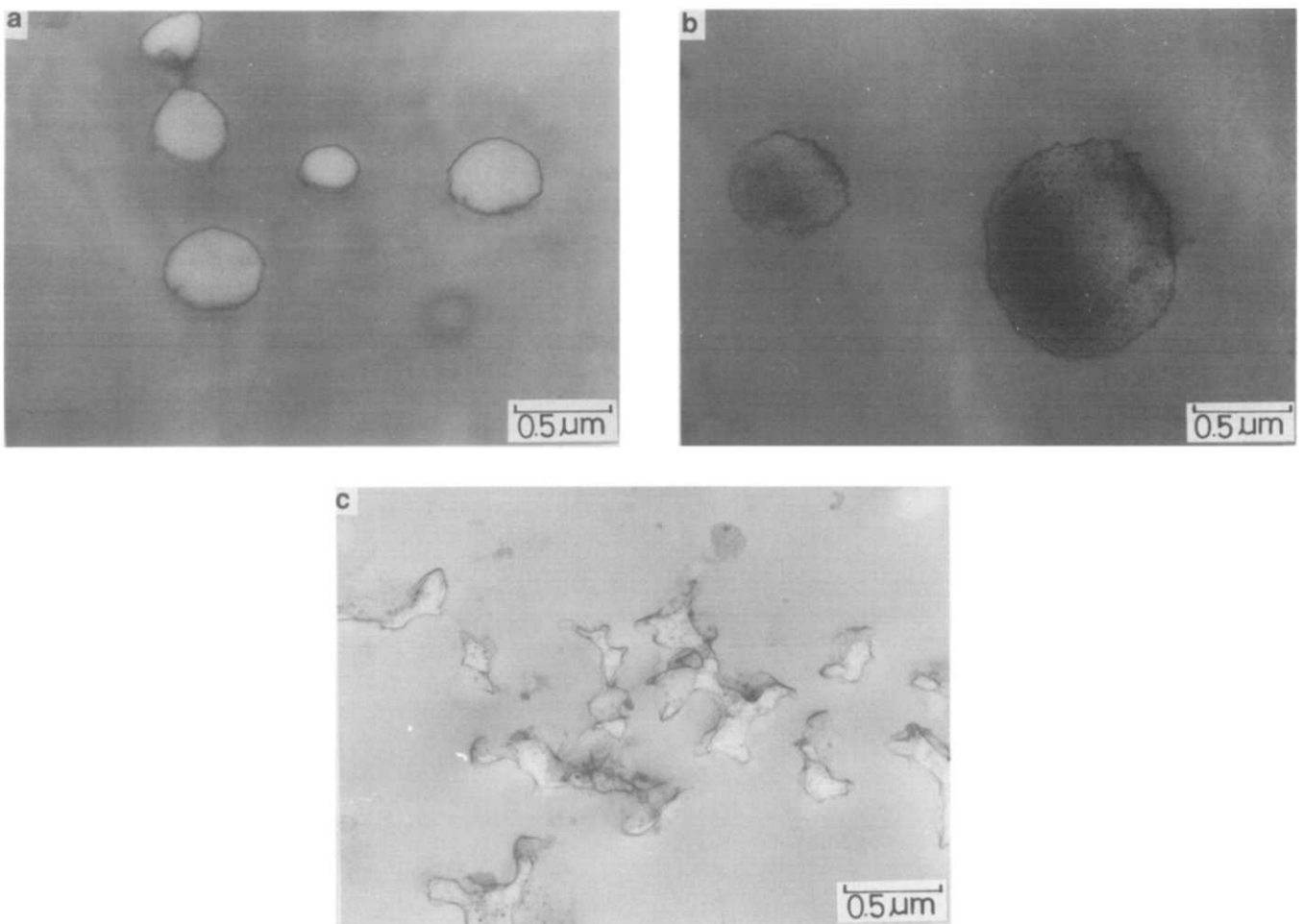


Figure 3 TEM micrographs of RuO_4 stained thin sections of 20 wt% modified epoxy resins: (a) modified with PBA; (b) P(BA-GMA) (95/5 mole ratio); (c) P(BA-1G) (95/5 mole ratio)

which accord with those observed by SEM (Figures 2a and b). In the P(BA-1G) modified resin (Figure 3c), irregularly shaped domains were observed. Moreover, in the P(BA-GMA) and the P(BA-1G) modified resins (Figures 3b and c), microphase separation structure was observed in the domains.

Figure 4 shows the dynamic mechanical properties of the unmodified and the 20 wt% modify epoxy resins. The sharp peaks in $\tan \delta$ at 120–150°C are due to the glass transition temperature (T_g) of the cured epoxy matrix. In the unmodified resin, the broad peak of $\tan \delta$ at about -60°C is due to the β relaxation of the cured epoxy

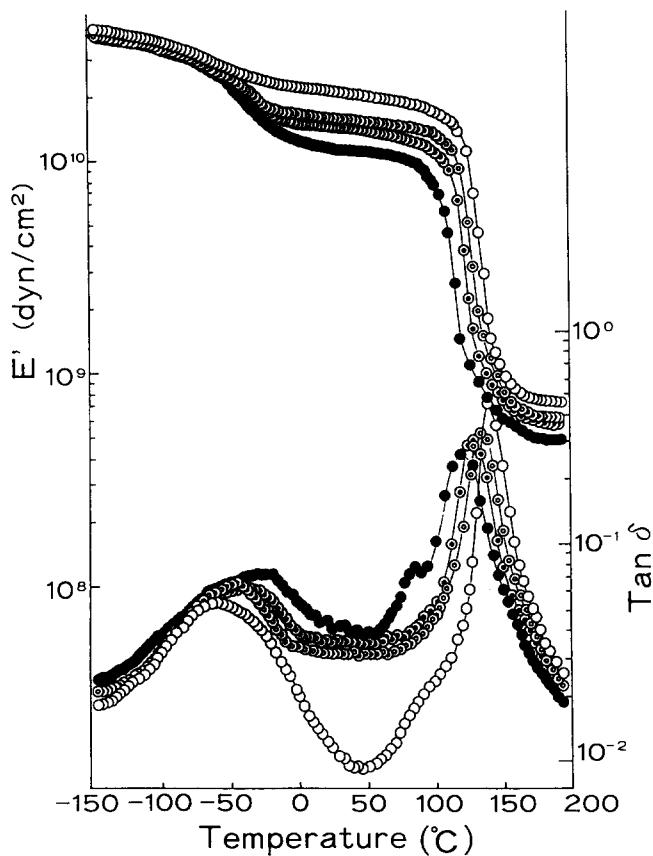


Figure 4 Dynamic mechanical properties of unmodified cured epoxy resin (○) and resins 20 wt% modified with PBA (●), P(BA-GMA) (95/5, mole ratio) (⊙) and P(BA-1G) (95/5, mole ratio) (⊖) produced by *in situ* u.v. radiation polymerization

matrix. In the PBA modified resin, a broader peak of $\tan \delta$ is observed at about -50°C , which is due to the T_g of PBA. The $\tan \delta$ peak in the low temperature region is broader and shifts to higher temperature in the order P(BA-1G) > P(BA-GMA) > PBA modified resin. The $\tan \delta$ values in the range $0-80^{\circ}\text{C}$ were ranked in the order P(BA-1G) > P(BA-GMA) > PBA > unmodified resin.

Figure 5 shows the relationships between acrylic polymer content and storage modulus (E') at 25°C and the T_g values of the cured epoxy matrix, which were obtained from the dynamic mechanical curves of Figure 4. Both E' and T_g decrease with increasing acrylic polymer content in the order P(BA-1G) > P(BA-GMA) > PBA modified resin. The calculated concentrations of acrylic polymer in epoxy matrix at 20 wt% are 2.5, 3.3 and 6.5 wt% for PBA, P(BA-GMA) and P(BA-1G), respectively. These values were calculated by assuming that the relation between T_g and acrylic polymer concentration in epoxy matrix is additive and by using the measured T_g values (Figure 4). This indicates that the apparent miscibility of the acrylic polymer and the epoxy matrix is higher in the order P(BA-1G) > P(BA-GMA) > PBA modified resin. This is also supported by the results shown in Figures 2-4.

Figure 6 shows the internal stress, which decreases with increasing acrylic polymer content. The tendency is more marked in the order of P(BA-1G) > P(BA-GMA) > PBA modified resin.

Figure 7 shows the thermal expansion coefficient (α_1) below T_g of the cured epoxy resin. In the three types of modified resin, α_1 increases with increasing acrylic

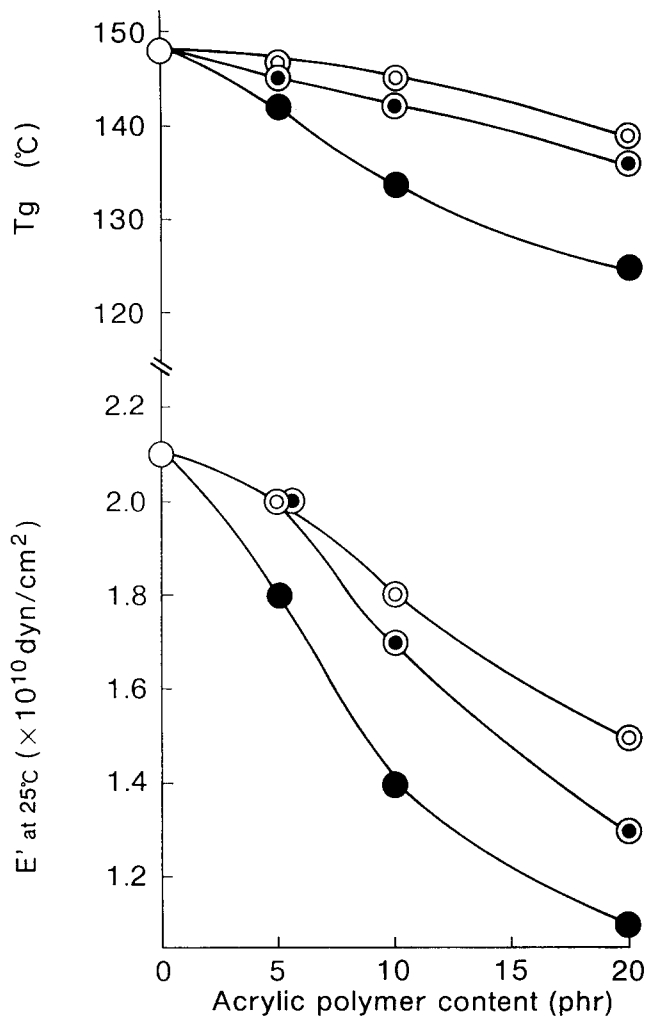


Figure 5 Storage modulus (E') at 25°C and T_g of unmodified cured epoxy resin (○) and resins modified with PBA (●), P(BA-GMA) (95/5, mole ratio) (⊙) and P(BA-1G) (95/5, mole ratio) (⊖) produced by *in situ* u.v. radiation polymerization

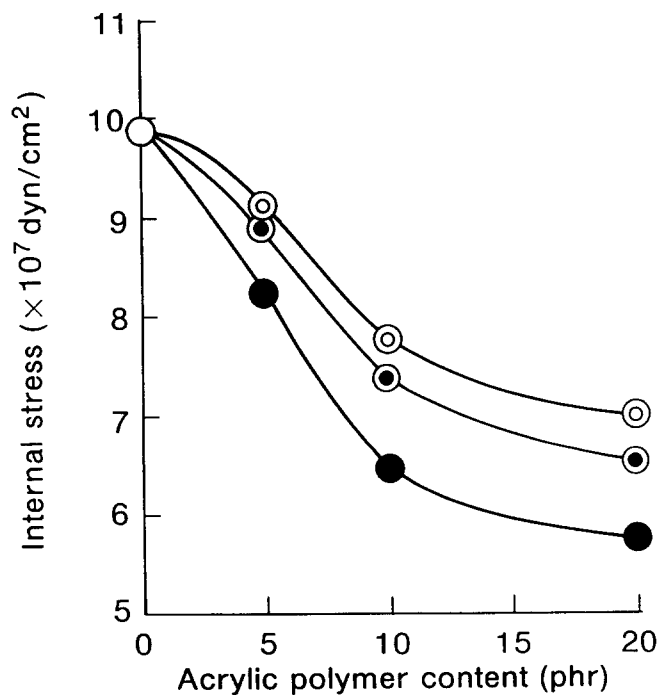


Figure 6 Internal stress of unmodified cured epoxy resin (○) and resins modified with PBA (●), P(BA-GMA) (95/5, mole ratio) (⊙) and P(BA-1G) (95/5, mole ratio) (⊖) produced by *in situ* u.v. radiation polymerization

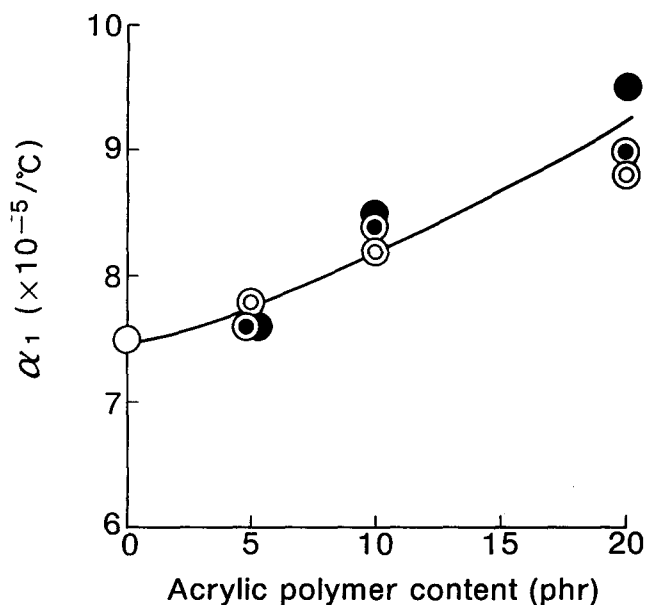


Figure 7 Thermal expansion coefficient (α_1) below T_g of unmodified cured epoxy resin (○) and resins modified with PBA (⊙), P(BA-GMA) (95/5, mole ratio) (⊖) and P(BA-1G) (95/5, mole ratio) (●) produced by *in situ* u.v. radiation polymerization

polymer content and the degree of increase is almost the same.

As described in previous papers by us¹⁵ and by others¹⁻³, the internal stress which results from the shrinkage occurring in the cooling process from cure temperature to room temperature was calculated by the following equation:

$$\sigma = \int_{25^{\circ}\text{C}}^{T_g} E'_{25^{\circ}\text{C}} (\alpha_1 - \alpha_a) dt \quad (1)$$

where σ is the internal stress, α_a is the thermal expansion coefficient of the aluminium plate and E' , T_g and α_1 are defined above. It is clear from the results shown in Figures 5-7 and equation (1), that the reduction of internal stress in the order P(BA-1G) > P(BA-GMA) > PBA modified resin is caused by the reduction of E' and T_g . That is, the introduction of functional groups to PBA by the copolymerization of GMA or 1G was useful in reducing internal stress.

However, the introduction of functional groups decreased T_g , and the heat resistance of the epoxy resin too, because the apparent miscibility of domains and epoxy matrix was increased. This may be undesirable for the

application of epoxy resin. Accordingly, the formation of domains consisting of low T_g polymer which is immiscible and interacts strongly with epoxy resin at the interface layer seems to be useful in reducing internal stress without lowering the good heat resistance of epoxy resin. In a previous paper¹¹, we reduced the internal stress without reducing T_g by using acrylic core-shell particles containing functional groups produced by seeded emulsion polymerization. In those cases, the miscibility between domains and epoxy matrix seems to be limited at the interfacial layer. This point will be clarified in a subsequent paper¹⁸.

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