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Internal stress of epoxide resin modified with spiro ortho-ester type resin

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The internal stress and shrinkage of bisphenol type epoxide resin compounded with spiro ortho-ester resin were investigated by measuring the change of density and the strain of the steel ring embedded in the cured resins. Internal stress was absent in the rubbery region and was mainly induced by shrinkage in the glassy region. The shrinkage in the glassy region seems to be directly converted to internal stress because the motion of network segments is restricted in this region. The internal stress decreased with increasing fraction of spiro ortho-ester resin in the cured system. The reduction of internal stress was independent of the expansion of the cured resin caused by the reaction of spiro rings during the curing process. This reduction was due to the decrease in the glass transition temperature T_g of the cured resins, that is the decrease in the shrinkage occurring in the cooling process from T_g to room temperature.

1. Introduction

Thermosetting resins such as epoxide resin usually shrink during the curing and cooling processes. Thus, an internal stress occurs in the cured resins. The internal stress causes various defects, e.g. crack, void, delamination, and reduction of quality in the fields of moulding, coating, adhesion, lamination, and composite properties. Accordingly, it is one of the most important subjects in this field to prevent or decrease the occurrence of shrinkage and internal stress.

It has been reported that internal stress is affected by the glass transition temperature [1–3], modulus [4, 5] and rigidity [6] of the cured resins. However, many problems still remain for the investigation of internal stress. For example, the reported values of internal stress show large difference for each investigator, ranging from 5.06 MPa [7] to 0.32 MPa [8] for the same epoxide resin cured with ethylenediamine. In addition, it is usually believed that the addition of mineral filler reduces the internal stress of cured resins. However, it was found in our investigation [9, 10] that the shrinkage of cured epoxide resin is decreased, but the internal stress is not always decreased by loading the mineral filler.

In previous papers, we have pursued the mechanism for the occurrrence of internal stress and some plans to reduce or prevent internal stress in both bulk [9–16] and coatings [17–20] of epoxide resins cured with various curing agents [9–13, 15–17] and catalysts [14–16], and filled with minerals [9, 10], reactive rubbers [14], plasticizers [20] and reactive diluents [17].

Monomers such as spiro ortho-esters [21, 22] and bicyclo-esters [23, 24] that expand or contract little during the polymerization process were recently developed. Since these monomers can be reacted with epoxide resins through anhydride curing agents, addition of these uncontractable monomers may reduce the internal stress in the curing epoxide resins.

In the present paper, the effects of the addition of uncontractable monomer having spiro rings on the internal stress of cured epoxide resins were investigated in detail. The mechanism for

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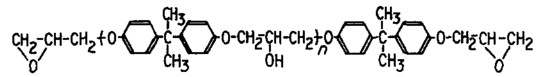
the decrease of shrinkage and internal stress was also pursued.

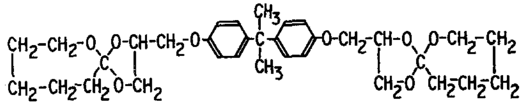
2. Experimental details

2.1. Materials

The epoxide resin used was a liquid bisphenol type epoxide resin (BADGE, epoxide equivalent 190 ± 5; $\bar{M}_n = 380$, Epikote 828):



and the spiro ortho-ester resin used was bisphenol *A* dispiro ortho-ester (SOE, spiro ring equivalent 380; EXP 101):



Hexahydrophthalic anhydride (HHPA) and 2-ethyl-4-methyl imidazole (EMIM) were used as curing agent and accelerator, respectively. The curing agent and accelerator were EP grade materials and were used without further purification.

2.2. Curing of epoxide resin

Various amounts of spiro ortho-ester resin were added to epoxide resin and the mixtures were stirred at 80° C. Stoichiometric amounts of curing agent and 1.8 phr of accelerator were compounded with the mixtures. The compounds were poured into silicon moulds, degassed, and allowed to cure. The curing was carried out for 2 h at 130° C and then for 2 h at 180° C in a forced-draught oven. It was confirmed that the conversion of the epoxide group could not be increased with further curing.

2.3. Measurements

The shapes and the dimensions of specimens for measuring internal stress are shown in Fig. 1a. The steel ring was placed on the silicon rubber mould. The compounds of epoxide resin, spiro ortho-ester resin, curing agent, and accelerator were cast into the space between the steel ring and the outer frame. The strain gauge (KFC–10–C–1–11, Kyowa Electric Co.) was bonded to the interior side of steel ring (thickness 0.5 mm) by using adhesives.

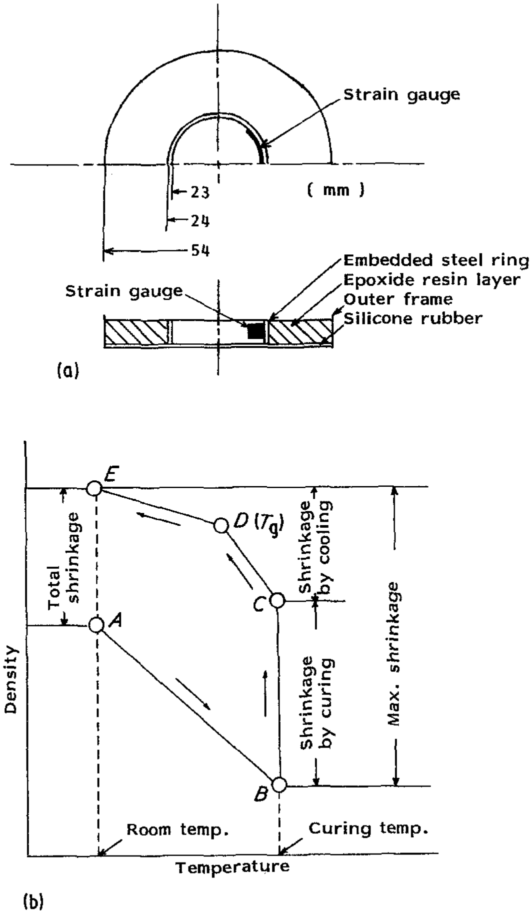


Figure 1 (a) Test specimen for internal stress measurement; (b) curing cycle of epoxide resins.

As the cured epoxide resins are formed during the progress of curing, the steel ring is subject to stress and gives rise to strain [25–27]. The strain δ_θ in the steel ring was measured after removing the silicon rubber mould. To cancel the thermal expansion of the ring, the thermal strain δ_t of the steel ring was subtracted from the value of δ_θ. The internal stress σ_i was calculated by using the equation [28]

$$\sigma_i = Ed(\delta_\theta - \delta_t)/r$$

where *E*, *d*, and *r* are the modulus, thickness and inside diameter of the steel ring, respectively.

The diagram of the curing cycle is illustrated schematically in Fig. 1b. The sample at Point *A* is the initial compound. This sample is heated to the curing temperature (180° C) and begins to react at Point *B*. The reaction is completed at Point *C*. From Point *C*, the sample is cooled to room temperature (Point *E*) through the glass

TABLE I Estimation of internal stress generated in cured epoxide resins

SOE/BADGE ratio	T_g (°C)	Network chain concentration, ν (mol cm^{-3}) × 10^3	Shrinkage in glassy region (%)	Internal stress σ_i (MPa)	σ^*_{calc} (MPa)	σ_{calc}/σ_i
100/ 0	58	1.75	0.9	0.9	4.5	3.75 ± 1.35
75/ 25	68	1.94	1.3	2.3	8.3	
50/ 50	96	2.18	2.5	4.0	16.0	
25/ 75	111	2.32	2.8	5.3	13.7	
0/100	134	2.67	3.7	6.8	21.0	

*From Equation 2.

transition temperature (T_g, Point *D*). The curing cycle is completed in Point *E*.

The volume of contraction during the cooling process was calculated from the density change of the cured system, according to the following equations [29]:

$$\alpha_r = \frac{1/\varrho_{s(T_g)} - 1/\varrho_{s(t)}}{1/\varrho_{s(t)}} \times 100$$

$$\alpha_g = \frac{1/\varrho_{s(r)} - 1/\varrho_{s(T_g)}}{1/\varrho_{s(t)}} \times 100$$

where α_r and α_g are the shrinkage in the rubbery (*C–D*) and glassy (*D–E*) regions. $\varrho_{s(t)}$, $\varrho_{s(T_g)}$ and $\varrho_{s(r)}$ denote the density of the solid resin at curing, at the glass transition, and at room temperature, respectively.

Dynamic mechanical properties were determined using an inverted, free-oscillation torsion pendulum (RD–1100 AD, Rhesca Co.) according to ASTM D 2236–64T. The frequency of oscillation was adjusted to remain within the range of 0.3 to 3.0 Hz. The heating rate used was 1° C min^{-1} *in vacuo*.

3. Results and discussion

3.1. Dynamic mechanical properties of cured epoxide resins

Dynamic mechanical properties of cured bisphenol type epoxide resins (BADGE) compounds with spiro ortho-ester type resin (SOE) are shown in Fig. 2. Since the measurements were carried out at 0.3 to 3.0 Hz, the temperature where the elastic modulus decreased drastically and the damping showed a maximum value was regarded as the glass transition temperature T_g. The T_g of each system is shown in Fig. 1b as T_{g_0}, $T_{g_{25}}$, $T_{g_{50}}$, $T_{g_{75}}$ and $T_{g_{100}}$. The suffixes mean the content (mol %) of SOE.

The T_g of the cured systems and the elastic modulus G_r in the rubbery ($> T_g$) region decreased with increase in the SOE content. The concentration of the network chains ν can be calculated from the G_r at 40° C above T_g using the equation of rubber elasticity [30, 31] (Table I).

γ relaxations were clearly observed at about -130° C in the damping curves of SOE-compounded systems. The peak height of this relaxation increased with increase in the content of SOE. It has already been reported that the γ relaxation is due to the motion of four or more methylene units [32]. Accordingly, it is expected that the γ relaxation of these systems is caused by the motion of methylene sequences included in SOE. This result shows that spiro ortho-ester resin is incorporated in the epoxide resin network.

Plots of T_g against SOE/BADGE ratio are shown in Fig. 3. There is an approximate linear relationship between T_g and SOE/BADGE ratio. This means that the T_g of the cured systems depends on the SOE content.

3.2. Internal stress in cured epoxide resins

The changes in the magnitude of the internal stress σ_i during cooling from the curing temperature (180° C) to room temperature are shown in Fig. 4a. The internal stresses were generated near T_g of each cured system, and increased linearly with decreasing ambient temperature.

The internal stress–temperature plots constructed by regarding T_g as the starting point are shown in Fig. 4b. The changes in the internal stress appeared to be represented by a straight line, even if the SOE content, T_g (Fig. 2, Table I), and ν (Table I) of the cured epoxide resins were different in each system.

The results of Fig. 4 mean that internal stresses are almost absent in the rubbery ($> T_g$)

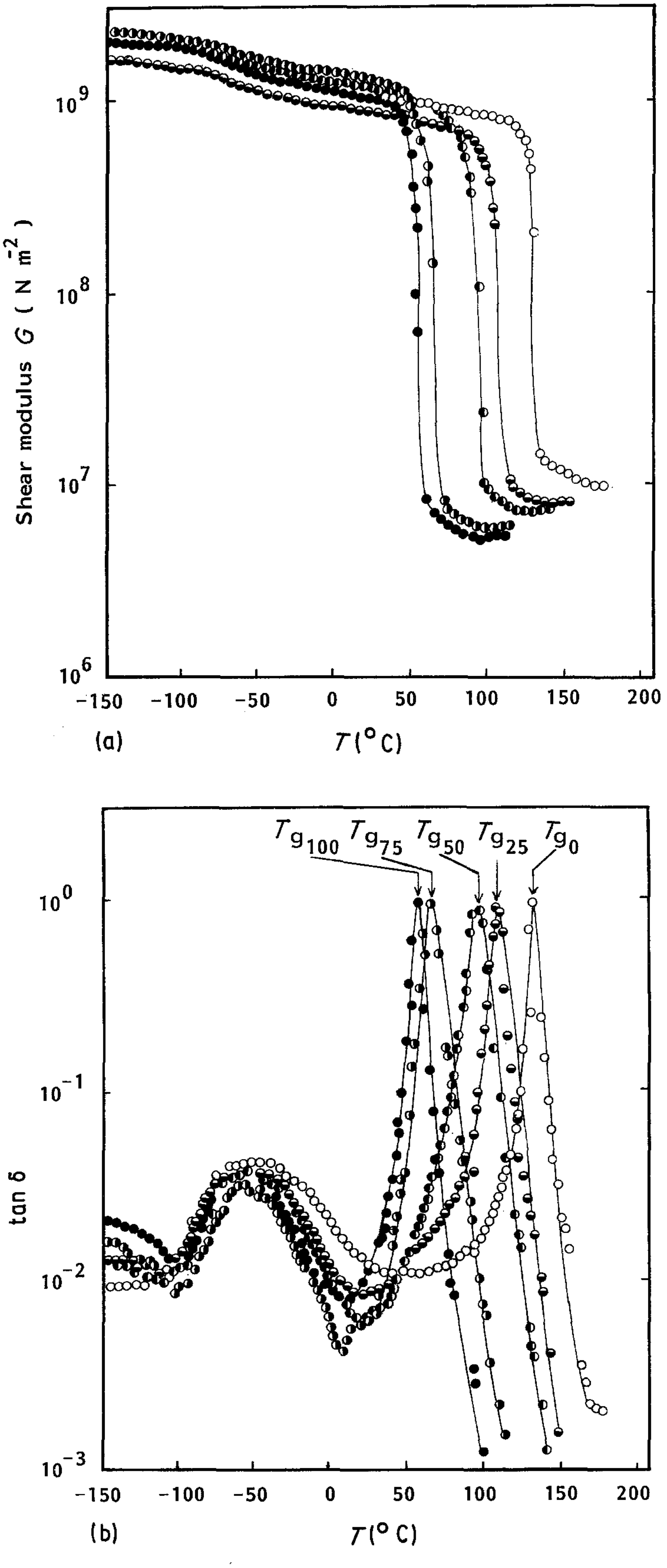


Figure 2 Dynamic mechanical properties of cured epoxide resins. Epoxide resin BADGE (bisphenol *A* DGE, Epikote 828); additive SOE (spiro ortho-ester, EXP 101); curing agent HHPA (hexahydrophthalic anhydride); accelerator EMIM (2-ethyl-4-methyl imidazole). (a) Shear modulus; (b) tan δ. Values of SOE/BADGE ratio and T_g as follows: ● 100/0, 58° C; ◑ 75/25, 68° C; ◐ 50/50, 96° C; ◒ 25/75, 111° C; ○ 0/100, 134° C.

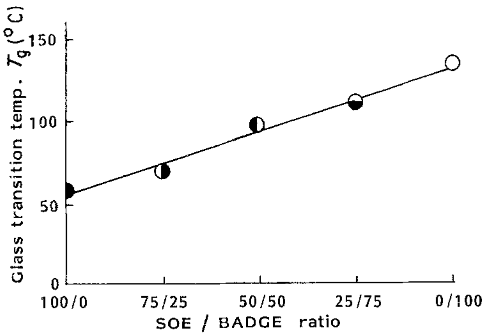


Figure 3 Glass transition temperature and SOE/BADGE ratio of cured epoxide resins. Notations as in Fig. 2. Epoxide resin BADGE, additive SOE; curing agent HHPA, accelerator EMIM.

region, and they increase in proportion to the decrease in the ambient temperature in the glassy ($< T_g$) region. Thus, the internal stresses at room temperature depend on the temperature difference between T_g and room temperature, as shown in Fig. 5a.

The relation between the values of internal stress at room temperature and the SOE/BADGE ratios of the cured systems is shown in Fig. 5b. The internal stresses depend on the composition of the cured resins. This result is expected, because the internal stress is proportional to the temperature difference between T_g and room temperature (Fig. 5a), and the T_g of the cured systems decreases with increasing content of SOE (Fig. 3). Accordingly, a lowering of the glass transition temperature is effective in decreasing the internal stress generated in the cured system.

3.3. Shrinkage in cured epoxide resins

The shrinkages of the cured systems during cooling from the curing temperature (180° C) to room temperature are shown in Fig. 6a. For all cured systems, the shrinkage from the curing temperature to T_g of each system (T_{g100}, T_{g75}, T_{g50}, T_{g25}, and T_{g0}) are shown by a straight line. Therefore, it is clear that the shrinkage of these systems in the rubbery region behaves in a similar manner, even though the content of SOE (Fig. 3), T_g (Fig. 2 and Table I), and ν (Table I) are different in each system.

However, the behaviour of the shrinkage in the glassy region is different from that in the rubbery region. The plots of shrinkage in the glassy region against temperature are shown in Fig. 6b. As the glass transition temperatures of these cured systems are different from each other (Fig. 2), the shrinkage in the glassy region arises at different temperatures, that is at the T_g of each system. In this plot, the dependences of shrinkage on the temperature were nearly constant in all systems.

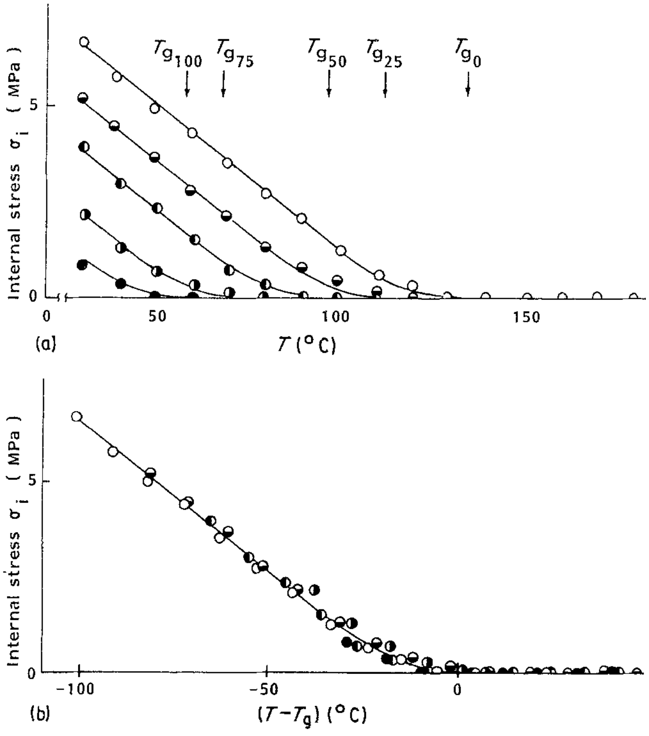


Figure 4 Internal stress of cured epoxide resins. Notations as in Fig. 2. Epoxide resin BADGE; additive SOE; curing agent HHPA; accelerator EMIM. (a) Internal stress against T, and (b) against $(T - T_g)$.

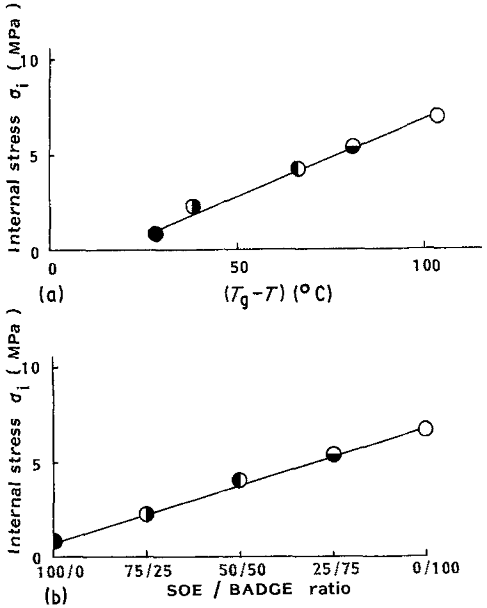


Figure 5 Interrelation between internal stress, temperature difference from T_g to room temperature, and SOE/BADGE ratios of cured epoxide resins. Notations as in Fig. 2. Epoxide resin BADGE; additive SOE; curing agent HHPA; accelerator EMIM. (a) Internal stress against $(T_g - T)$, and (b) against SOE/BADGE ratio.

To compare the behaviour of shrinkage in these systems the shrinkage–temperature plots, rewritten by considering the T_g of each system as a starting point, are shown in Fig. 6c. The relationship between the shrinkage in the glassy region and the temperature difference from T_g $(T - T_g)$ could be expressed by a straight line for all cured systems. It was concluded that the shrinkage in the glassy region increases at a constant ratio with decrease in the ambient temperature, regardless of the content of SOE in the cured resins. Thus, the shrinkage at room temperature depends on the temperature difference from T_g to room temperature $(T_g - T)$, as shown in Fig. 7a.

The relation between shrinkage in the glassy region and the SOE/BADGE ratios of the cured systems is shown in Fig. 7b. The shrinkage in the glassy region increased linearly with decrease in the content of SOE. Thus, the shrinkage of the cured BADGE system is significantly higher than that of the cured SOE system. This result is reasonable, since the linear shrinkage in the glassy region is proportional to the temperature difference from T_g to room temperature (Fig. 7a), and the T_g of the cured system increases with decrease in the content of SOE.

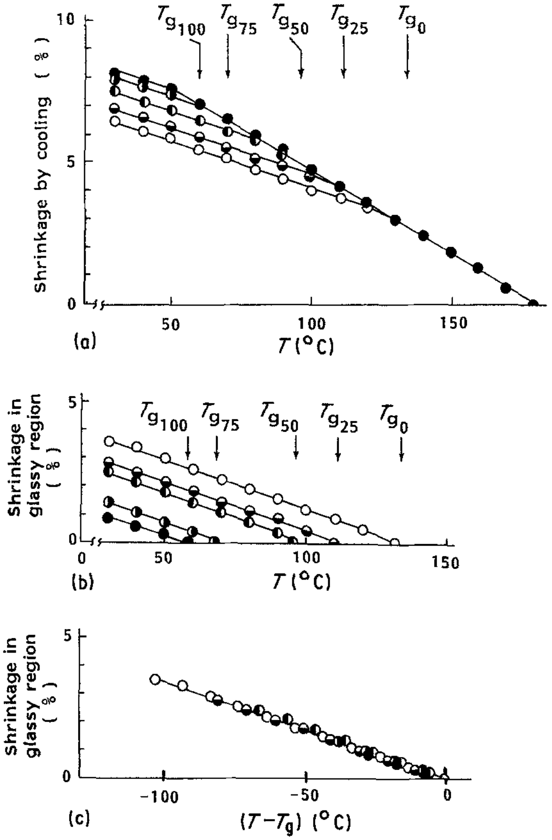


Figure 6 Shrinkage of cured epoxide resins. Notation as in Fig. 2. Epoxide resin BADGE; additive SOE; curing agent HHPA; accelerator EMIM. (a) Total shrinkage against temperature; (b) shrinkage in glassy region; (c) shrinkage against $(T - T_g)$.

3.4. Mechanisms for occurrence of internal stress and their estimation

Both the internal stress and shrinkage of cured epoxide systems compounded with SOE depended on the temperature difference from T_g, as shown in Figs. 4 and 6 respectively. Furthermore, little internal stress was generated in the rubbery region. Accordingly, the relation between internal stress and shrinkage in the glassy region should be investigated to pursue the mechanism for the occurrence of internal stress.

The relationship of internal stress to shrinkage in the glassy region is plotted in Fig. 8. An approximately linear relationship existed between the shrinkage and the internal stress in the glassy region for all cured systems. This result is in good agreement with that of previous papers for the bisphenol type epoxide resins cured with various curing agents [9–13, 15–17] and catalysts [14–16], and modified with various

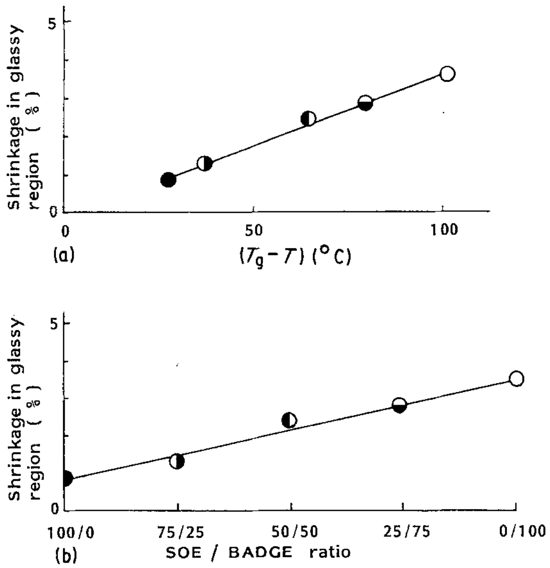


Figure 7 Interrelation between shrinkage in glassy region and temperature difference from T_g to room temperature and SOE/BADGE ratios of cured epoxide resins. Notation as in Fig. 2. Epoxide resin BADGE; additive SOE; curing agent HHPA; accelerator EMIM. (a) Shrinkage against $(T_g - T)$, and (b) against SOE/BADGE ratio.

fillers [9–10, 14], reactive diluents [17] and plasticizer [20].

The cured resins shrink clearly in the rubbery region (Fig. 6a). However, internal stress is almost absent in this region (Figs. 4a and b). These results are interpreted as showing that the motion of the network segments was facile and the cured resins could relax the shrinkage in this region. On the other hand in the glassy region the shrinkage is directly converted to internal stress (Fig. 8), because the motion of the network segments is restricted in this region.

The internal stress of the cured systems modified with SOE decreases with increase in the content of SOE (Fig. 5b). This reduction of the internal stress is independent of the expansion of SOE by the reaction of spiro rings during the curing process, because the internal stress depends directly on the shrinkage during the cooling process below the T_g of each system. We consider that the reduction of internal stress is due to the decrease of T_g of the cured resins with increasing content of SOE (Fig. 3), since the internal stress depends on the temperature difference from T_g (Fig. 5a).

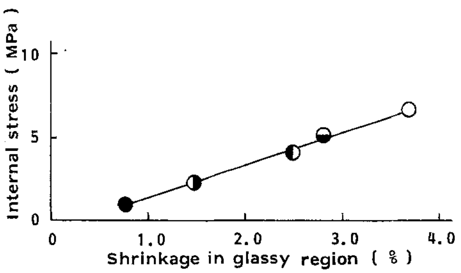


Figure 8 Internal stress against shrinkage in glassy resin of cured epoxide resins. Epoxide resin BADGE; additive SOE; curing agent HHPA; accelerator EMIM. Notation as in Fig. 2.

Estimation of internal stress induced in the cured system modified with SOE is shown in Table I. The internal stress is directly proportional to the shrinkage in the glassy region (Fig. 8). Thus, if we assume that the shrinkage in the glassy region is completely restricted by embedding a steel ring in the resins, it should be possible to calculate this stress from the thermal coefficient of expansion and the Young's modulus of the cured resins. If β_r is the linear expansion coefficient of the cured resins, β_s that of the steel ring, E the Young's modulus and T the temperature, the internal stress σ_{calc} is calculated from

$$\sigma_{calc} = \int_{30}^{T_g} E(\beta_r - \beta_s)\, dT \qquad (1)$$

The shear modulus G, rather than Young's modulus E, of cured resins was measured in this work (Fig. 2). The value of E in Equation 1 could be calculated from G by using an assumed value of 0.33 for Poisson's ratio. Accordingly, Equation 1 can be rewritten as follows:

$$\sigma_{calc} = \int_{30}^{T_g} 2.66G(\beta_r - \beta_s)\, dT \qquad (2)$$

The values of σ_{calc} estimated from the above equation are also shown in Table I. The ratio of the calculated internal stress to the experimental value is about 3.8 ± 1.3 for all cured systems. We consider that the difference between the calculated and experimental values of the internal stress is caused by assuming that the shrinkage in the glassy region is completely restricted by the steel ring embedded in the cured resins. To estimate exactly the internal stress, the degree of the restriction for shrinkage in the glassy region should be considered.

4. Conclusion

Bisphenol type epoxide resin compounded with spiro ortho-ester type resin, which expands or contracts little during the curing process, was cured with hexahydrophthalic anhydride. The magnitude of the internal stress and the mechanism for the occurrence of it were investigated in detail. The following conclusions were obtained:

(a) Internal stress is almost absent in the rubbery region and is mainly induced by shrinkage in the glassy region. This means that though the internal stress is easily relaxed in the rubbery region by the motion of network segments, the shrinkage in the glassy region is directly converted to internal stress because the motion of network segments is restricted in this region.

(b) Internal stress, shrinkage in the glassy region and the glass transition temperature of the cured resins decreased linearly with increasing fraction of spiro ortho-ester type resin in the cured system.

(c) Both internal stress and shrinkage in the glassy region depend on the temperature difference from T_g to room temperature. Accordingly, a decrease of the glass transition temperature is effective for reduction of the internal stress of the cured systems.

(d) Internal stress decreased with increasing fraction of spiro ortho-ester resin in the cured system. The reduction of internal stress is independent of the expansion of the cured resin caused by the reaction of spiro rings during the curing process. This reduction is due to the decrease in T_g of the cured systems, that is the decrease in the shrinkage occurring in the cooling process from T_g to room temperature.

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