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

Part 2 *Relation between internal stress and phase structure*

MITSUKAZU OCHI, KENICHI YAMAZAKI, MASAKI SHIMBO
Department of Applied Chemistry, Faculty of Engineering, Kansai University, Suita-shi, Osaka 564, Japan

Bisphenol-A type epoxide resin modified with various amounts of spiro ortho-ester (SOE) resin was cured with an imidazole. Internal stress of the modified systems decreased with increasing fraction of SOE resin in the cured resins. In particular, a drastic reduction of the internal stress was observed in the systems modified with more than 33 mol% SOE resin. In addition, heterogeneous structure was observed with modifier content over 33 mol%, and the elastic modulus of these systems decreased step-wise with increasing ambient temperature. On the other hand, the systems in which the modifier content was less than 20 mol% had homogeneous structure and thus the modulus was considerably higher than that of the former systems. Consequently, it was concluded that the drastic reduction of the internal stress in the systems modified with more than 33 mol% SOE resin depends on the low elastic modulus caused by the formation of heterogeneous structure.

1. Introduction

It is well known that internal stress usually occurs in cured epoxide resins and causes various defects, e.g. crack, void, and delamination [1, 2]. It is, therefore, one of the most important subjects in the field of epoxide resin technology in preventing or reducing the internal stress of cured resins. We have studied the mechanism by which internal stress occurs in both castings [3–5] and coatings [6–7] based on epoxide resins. Thus, it has been clarified that the internal stress in cured epoxide resins is not caused by curing shrinkage with progress of the curing reaction, but by the cooling shrinkage from the glass transition temperature to room temperature during the cooling process after curing. Consequently, we concluded that (a) the decrease in the glass transition temperature, T_g, (b) the reduction of thermal expansion coefficient in glassy region, and (c) the decrease of modulus in glassy region of cured resins, are effective in reducing the internal stress in castings and coatings [6].

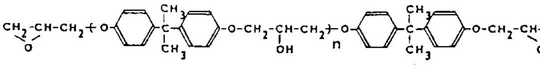
In a previous paper [8] we modified bisphenol-A type epoxide resin with spiro ortho-ester type resin which contracts little during the polymerization process [9], and thus could reduce the internal stress of the cured epoxide resins. However, the reduction of internal stress by this modification was not due to the reduction of the curing shrinkage, but due to a decrease in T_g of the modified systems. A decrease in T_g of the cured resins is usually undesirable in their applications, because of the reduction of thermo-resistance.

In the present paper, epoxide resins are modified with spiro ortho-ester type resin and a method for reducing the internal stress without decreasing T_g of these modified resins is pursued.

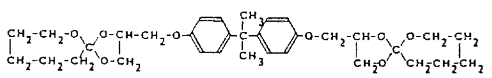
2. Experimental details

2.1. Materials

The epoxide resin used was a liquid bisphenol-A type resin (DGEBA, epoxide equivalent: 190 ± 5, Epikote 828, Structure I) and the spiro ortho-ester resin used was a bisphenol-A dispiro ortho-ester (SOE resin, spiro ring equivalent: 380, EXP-101, Structure II).



Structure I



Structure II

2-Ethyl-4-methyl imidazole (2E4MZ) was used as a catalytic curing agent. These resins and the catalytic curing agent are commercial grade and EP grade materials, respectively, and were used without further purification.

2.2. Curing of epoxide resin

Various amounts of SOE resin were added to epoxide resin and the mixtures were stirred at 80° C. Then 5 wt% 2E4MZ was compounded with the mixtures. The compounds were stirred at the same temperature *in vacuo*, until the curing agent dissolved completely in the epoxide resin, and were then poured into steel or (Frekote 44, Frekote Inc., Seabrook, USA). The curing was carried out at 130° C for 2 h followed by 180° C for 6 h. It was confirmed that the conversion of the epoxide group could not be increased with further curing.

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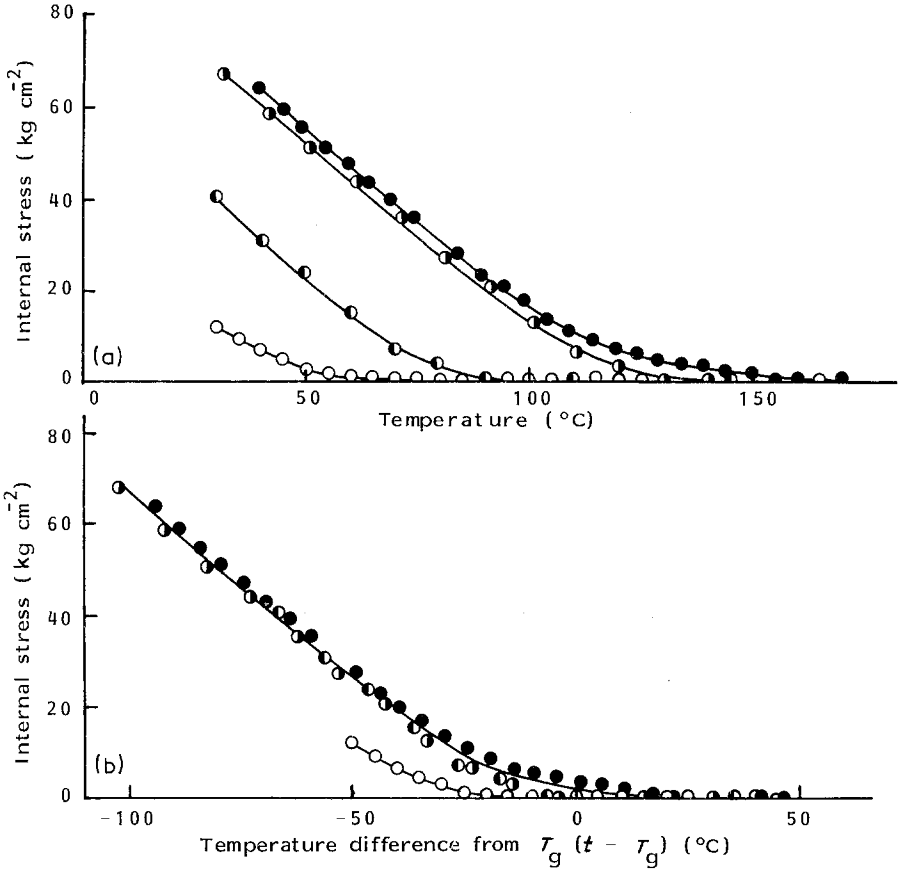


Figure 1 Internal stress of SOE-modified epoxide resin cured with acid anhydride and imidazole plotted against (a) temperature. (b) $t - T_g$. SOE resin (mol %) added for anhydride-cured systems: (◐) 0, (◑)50. SOE resin (mol %) added for imidazole cured systems: (●) 0, (○) 33.

2.3. Measurements

As the method for measuring the internal stress was described in detail in the previous paper [8], only an outline of this method is given here. A strain gauge (KFC-10-C-1-11, Kyowa Electric Co. Ltd, Tokyo, Japan) was bonded inside a steel ring. The steel ring-bonded strain gauge was placed on the mould coated with release agent and the epoxide resin compound was cast on the outside of the steel ring. As the cured epoxide resin was formed with the progress of curing, the steel ring was subjected to stress and thus strain. The change in the strain, δ_0, in the curing process was measured and the internal stress, σ_i, was calculated using the equation

$$\sigma_i = Ed(\delta_0 - \delta_t)/r$$

where E, d, and r are the modulus, the thickness, and the inside diameter of steel ring, respectively. δ_t is the thermal strain of steel ring itself and is subtracted from the value of δ_0 to cancel the thermal expansion or contraction of the ring.

The volume contraction during the cooling process was calculated from the density change of the cured system, according to the following equations [10]

$$\alpha_r = \frac{1/\varrho_{sT_g} - 1/\varrho_{st}}{1/\varrho_{st}} \times 100$$

$$\alpha_g = \frac{1/\varrho_{sr} - 1/\varrho_{sT_g}}{1/\varrho_{st}} \times 100$$

where α_r and α_g are the shrinkage in the rubbery and glassy regions. ϱ_{st}, ϱ_{sT_g}, and ϱ_{sr} 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-1100AD, Rhesca Co. Ltd, Tokyo, Japan) according to ASTM D 2236-70. The frequency of oscillation was adjusted to be within the range 0.3 to 3.0 Hz. Samples were heated at 0.7° C min^{-1} *in vacuo*.

3. Results and discussion

3.1. Comparison of internal stresses in anhydride-cured and imidazole-cured systems

The changes in magnitude of internal stresses, σ_i, in the unmodified and modified epoxide resins cured with anhydride or imidazole are shown in Fig. 1a. The data of the anhydride-cured systems are identical to those reported in the previous paper [8].

The magnitude of the internal stresses in the unmodified systems is nearly the same in both the anhydride- and the imidazole-cured systems. However, in the systems modified with spiro ortho-ester (SOE) resin, the internal stress of the imidazole-cured system is considerably lower than that of the anhydride-cured system. It has already been reported that the reduction of the internal stress in the anhydride-cured system is due to the decrease in glass transition temperature, T_g, by modification with the SOE resin [8]. Thus, to cancel the effect of T_g, the internal stresses of these systems were replotted by considering the T_g of each system as an original point, and are shown in Fig. 1b. In this figure, the internal stresses of the unmodified systems and the modified system cured with anhydride are shown by a curved line. This shows that the values of

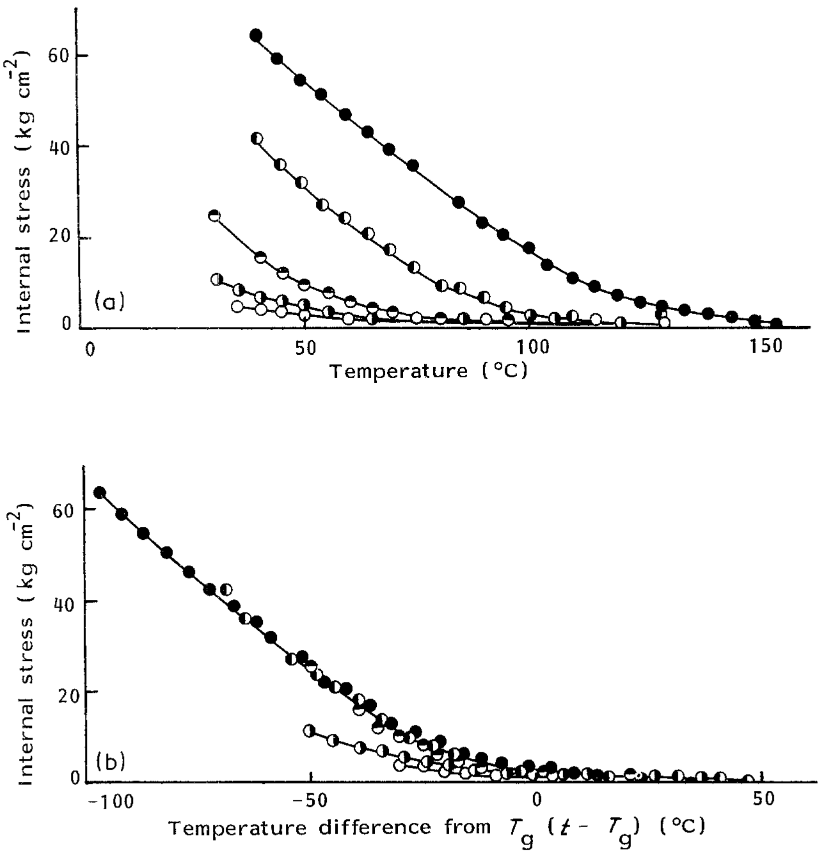


Figure 2 Internal stress of cured epoxide resin modified with SOE resin plotted against (a) temperature, (b) $t - T_g$. SOE resin added (mol %): (●) 0, (◐) 10, (◓) 20, (◑) 33, (○) 40. Curing catalyst: 2E4MZ.

the internal stress of these systems are determined by the T_g of the systems. But the internal stress of the modified system cured with imidazole is lower than that of other systems. Accordingly, we consider that the modification with SOE resin is more effective in reducing the internal stress in the imidazole-cured system and thus the mechanism for the reduction of the internal stress in this system is different from that in the anhydride-cured system.

3.2. Internal stress in the modified epoxide resin systems

Effect of SOE resin contents on the internal stress of the imidazole-cured systems is shown in Fig. 2a. The internal stress was generated near T_g of each cured system, and increased linearly with decreasing ambient temperature. Namely, the internal stress in the cured systems is almost absent in the rubbery ($> T_g$) region, and increases in the glassy ($< T_g$) region in proportion to the decrease in ambient temperature. This is natural, because the elastic modulus in the glassy region is about twenty times higher than that in the rubbery region.

In addition, the magnitude of the internal stress in these systems decreased with increase in SOE resin content. This shows that the modification with SOE resin is effective in reducing the internal stress of the cured epoxide resins. However, the values of internal stress are affected by the T_g of cured resins. To cancel the effect of T_g on the internal stress, the internal stress–temperature plots constructed by regarding T_g as an original point, are shown in Fig. 2b. When the SOE resin content is lower than 20 mol %, the changes in internal stress appeared to be represented by a curved line and the values of the internal stress increased rapidly with decreasing ambient temperature. On the other hand, in the systems modified with more than 33 mol % SOE resin, the internal stress is considerably lower than that of the former systems. This result shows that although the reduction of the internal stress in < 20 mol % SOE content is due to the decrease in T_g of the cured resin, an additional mechanism for reducing the internal stress exists in the system modified with > 33 mol % SOE resin.

3.3. Morphology of the modified epoxide resin systems

Dynamic mechanical properties of the cured epoxide resins compounded with SOE resin are shown in Fig. 3a and b. T_g of the cured systems and elastic modulus in the rubbery ($> T_g$) region decreased with increase in SOE resin content. These results are due to the formation of methylene sequences with the ring-opening polymerization of SOE resin and show that the SOE resin is incorporated in the epoxide resin network.

In the cured resins modified with less than 20 mol % SOE resin, the elastic modulus decreased sharply at the T_g of each system and the loss tangent showed one peak in the glass–rubber transition region. On the other hand, in the systems modified with > 33 mol % SOE resin, the elastic modulus decreased step-wise and the loss tangent revealed two peaks in the transition region. It is expected from these results that the latter systems are composed of heterogeneous structure, though the former systems consist of a homogeneous structure. Thus, we consider that the two peaks of loss tangent in the latter systems show the glass transition temperatures T_{gE} and T_{gS} for epoxide resin phase and SOE resin phase, respectively.

To confirm the phase structure of these systems,

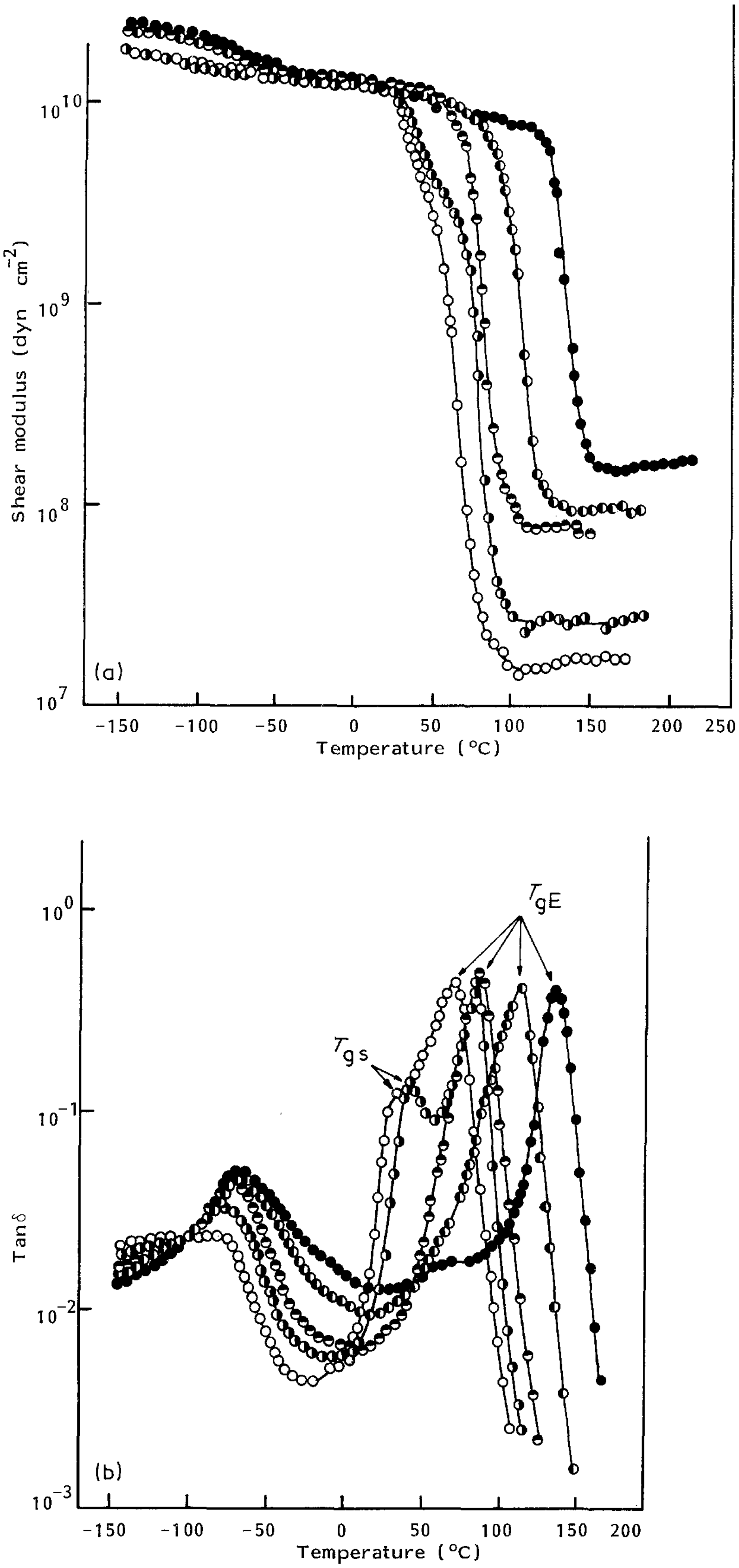
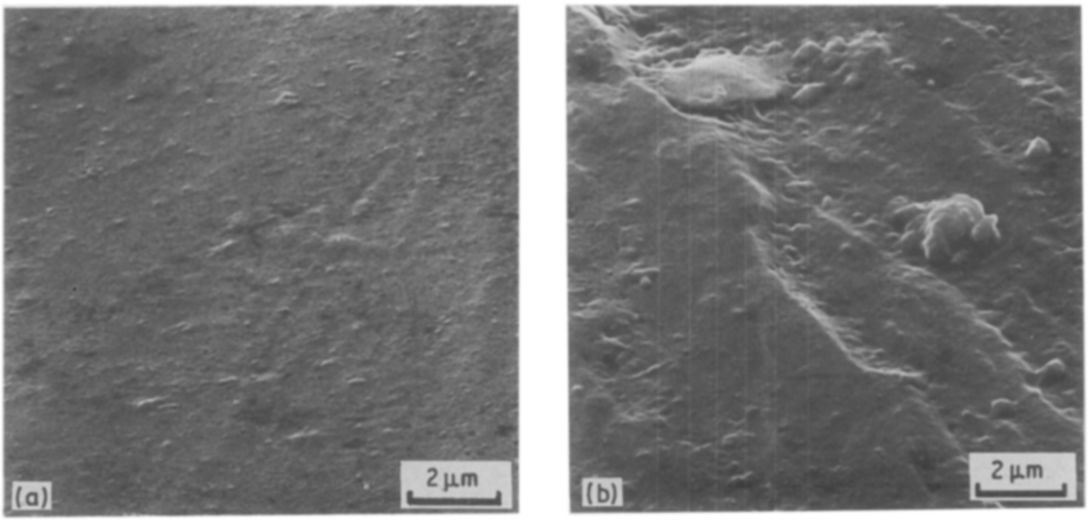


Figure 3 (a) Shear modulus–temperature plots for cured epoxide resins modified with SOE resin. For key, see Fig. 2. (b) Loss tangent–temperature plots for cured epoxide resins modified with SOE resin. For key, see Fig. 2.

scanning electron micrographs of their fracture surfaces are shown in Fig. 4. In the systems unmodified and modified with 20 mol % SOE resin, the morphology of their fracture surfaces was flat and uniform. In contrast, a heterogeneous structure was observed in the system modified with 33 mol % SOE resin. Accordingly, it is concluded that the cured resins in which the SOE content is < 20 mol % form the homogeneous structure and the heterogeneous structure is formed in the system compounded with > 33 mol % SOE. Moreover, we consider that the morphology change observed in the SOE-modified system is related to the drastic reduction of the internal stress shown in Fig. 1.

3.4. Mechanisms for reduction of internal stress

The shrinkages of the cured systems during cooling from the curing temperature (180° C) to room temperature are shown in Fig. 5. The shrinkage of these



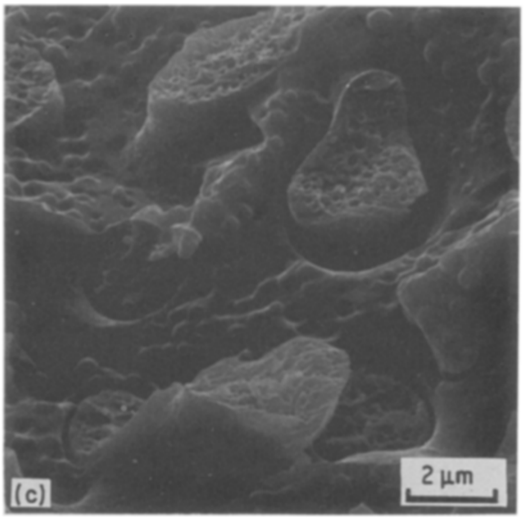


Figure 4 Scanning electron micrographs of the fracture surface of cured epoxide resins. Epoxide resin: Bisphenol-A DGE. Modifier: Bisphenol-A dispiro ortho ester. Curing catalyst: 2E4MZ. Spiro/epoxy ×4800 equivalent ratios: (a) 0/1.0, (b) 0.2/0.8, (c) 0.33/0.67.

systems increased with increasing SOE resin content. The shrinkage–temperature plots were represented by straight lines which have one or two flexion points for the cured systems modified with <20 mol % or >33 mol % SOE resin, respectively. The temperature where these flexion points were observed corresponds to the glass transition temperatures, T_{gE} and T_{gS} for the epoxide resin phase and the SOE resin phase. It is also concluded from this result that the heterogeneous structure is formed in the system modified with >33 mol % SOE.

The internal stress of these systems was produced during the cooling in the glassy ($<T_{gE}$) region (Fig. 2). To compare this with the internal stress, the shrinkages in the same region, replotted by considering the T_{gE} of each system as an original point, are shown in Fig. 6. The magnitude of shrinkage in the glassy region for the systems modified with >33 mol % SOE resin is higher than that for the system compounded with <20 mol % SOE resin. This shows that the former systems have a high thermal expansion coefficient in the temperature region from T_{gE} to T_{gS}.

The relationship between the internal stress and the shrinkage in the glassy region ($<T_{gE}$) is plotted in Fig. 7. The internal stress in the systems modified with <20 mol % SOE resin increased rapidly with increasing shrinkage in the glassy region, while in the systems

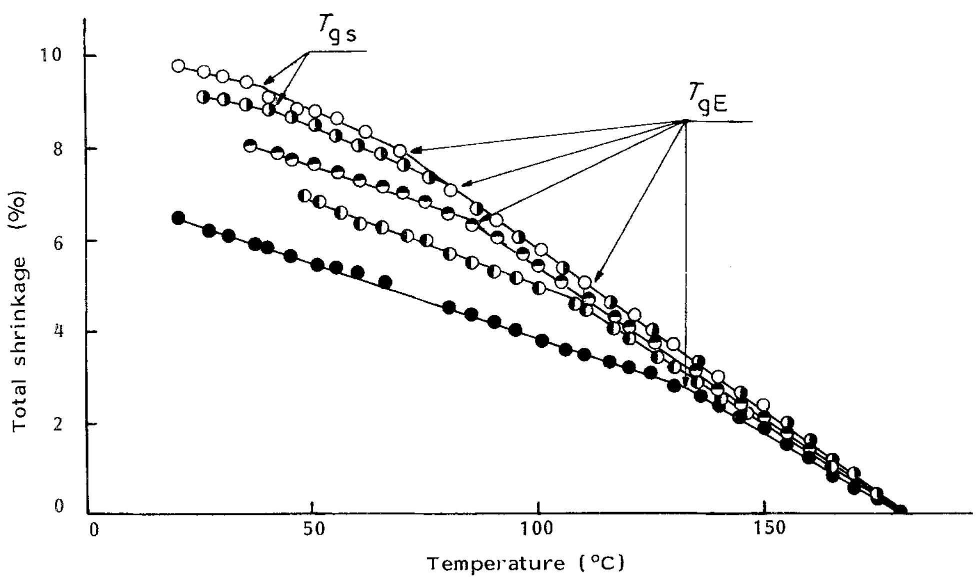


Figure 5 Total shrinkage of cured epoxide resins modified with SOE resin. For key, see Fig. 2.

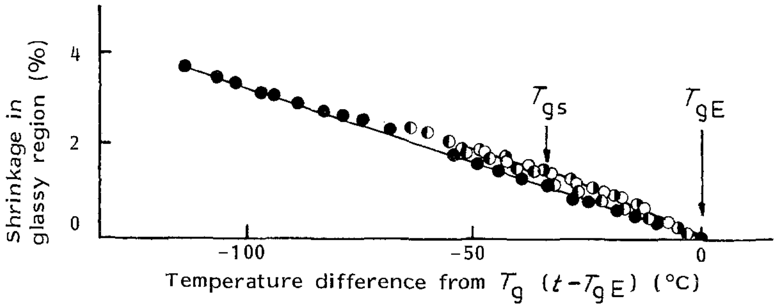


Figure 6 Shrinkage in the glassy region of cured epoxide resins modified with SOE resin. For key, see Fig. 2.

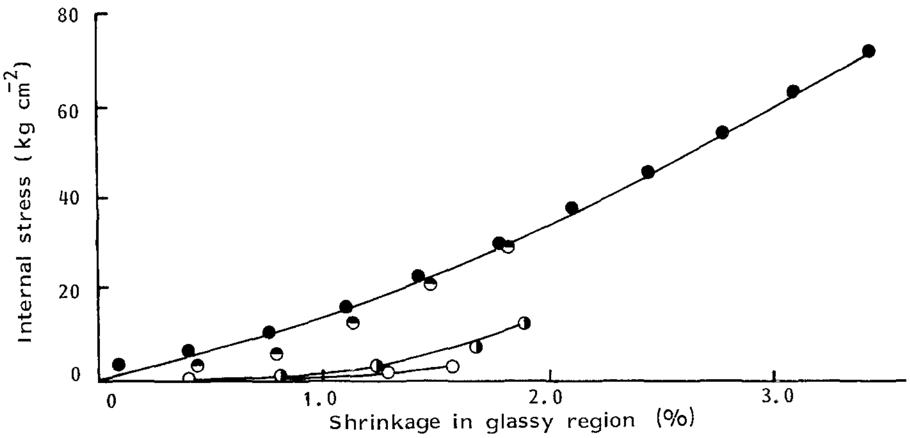


Figure 7 Relation between internal stress and shrinkage in the glassy region of cured epoxide resins modified with SOE resin. For key, see Fig. 2.

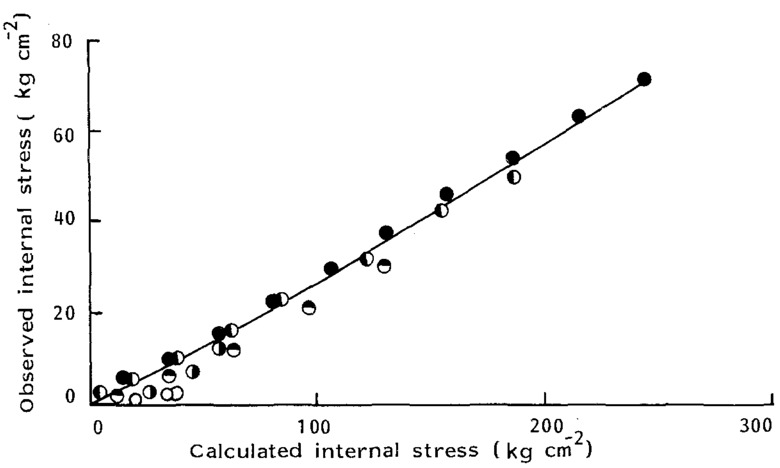


Figure 8 Relation between observed and calculated internal stresses of cured epoxide resins modified with SOE resin. For key, see Fig. 2.

modified with >33 mol % SOE resin, the internal stress increased little even if the shrinkage increased. Accordingly, it is considered that the shrinkage in the latter systems is converted to less internal stress, even if the cured resins contract at same degree during the cooling process. It has already been stated that the systems modified with > 33 mol % SOE resin form the heterogeneous structure and thus have a low elastic modulus in the temperature region T_{gE} to T_{gS} (Fig. 3). Thus, we conclude that the low internal stress in these systems is due to the low modulus in the glassy region.

If we assume that the shrinkage in the glassy region is completely restricted by the embedding of a steel ring and is completely converted to the internal stress, it should be possible to calculate the internal stress from the thermal expansion coefficient and the Young's modulus of the cured resins [6]. The relationship between the calculated internal stress, σ_{calc}, and the experimental value, σ_i, of the internal stress is shown in Fig. 8. An essentially linear relationship exists between the observed and calculated internal stresses regardless of SOE resin content. It is also confirmed from this result that the drastic reduction of the internal stress in the systems modified with > 33 mol % SOE resin is due to the low elastic modulus in the glassy region.

4. Conclusions

Bisphenol-A type epoxide resin modified with spiro ortho-ester resin was cured with 2-ethyl-4-methylimidazole. The magnitude of the internal stress and the mechanism for the reduction of the stress with this modification were investigated in detail. The following conclusions were obtained.

1. The morphology of the modified epoxide resins cured with imidazole was homogeneous in the region where the modifier content was < 20 mol %. When the content was > 33 mol %, the cured resins formed a heterogeneous structure.

2. Internal stress decreased with increasing fraction

of spiro ortho-ester resin in the cured resins. In particular, in the cured resins modified with > 33 mol % modifier, a drastic reduction of internal stress was observed.

3. In the system modified with < 20 mol % spiro ortho-ester resin, the reduction of internal stress is due to the decrease in T_g of the cured resins. When the modifier contents is > 33 mol %, the reduction of this stress depends on the low elastic modulus of the cured resins.

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