Internal Stress in Epoxide Resin Networks Containing Biphenyl Structure

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Synopsis

Bisphenol-A type and biphenyl type epoxide resins were cured with two types of aromatic diamines which have or do not have the carbon bridge between aromatic rings. Internal stress of these cured resins decreased with the introduction of a biphenyl structure into the networks. This reduction of the internal stress is attributed to the decrease of the elastic modulus in the glassy region caused by the low mobility of the biphenyl segment. On the other hand, the glass transition temperature increased with increasing the concentration of the biphenyl unit in the networks. These results revealed that the consistency of the decrease of the internal stress with the improvement of the heat resistance of the cured systems is possible by introducing the biphenyl structure to the epoxide resin networks.

INTRODUCTION

Epoxide resins are widely utilized as packaging and insulating materials and adhesives in the fields of electric and electronic industries. However, epoxide resins contract during the curing process, so that internal stresses arises in the cured resins.[1-3] These shrinkage and internal stresses cause the decrease of durability, such as a moisture and heat-cycle resistance of electric and electronic parts. Therefore, it is one of the most important subjects in the fields to prevent or reduce the shrinkage and internal stresses of cured epoxide resins.

In the previous studies,[4,5] we clarified that the internal stress mainly occurs during the cooling from the glass transition temperature T_g of cured resins to room temperature, and depends on both the elastic modulus and the thermal expansion coefficient of the cured resins in this temperature region. We also reported that internal stress could be reduced by modifying the epoxide resins with reactive elastomers,[6] thermoplastic polymers,[7] and uncontractable monomers such as a spiro-ortho-ester type resin.[8] However, these methods for reducing internal stress are not completely satisfactory because the modifications decrease the T_g, that is, the thermostability of the cured resins.

In the present work, the relationship between the internal stress and the chemical structure of epoxide resin networks was investigated in detail. A procedure to decrease the internal stress with no reduction of the T_g of cured resins was pursued.

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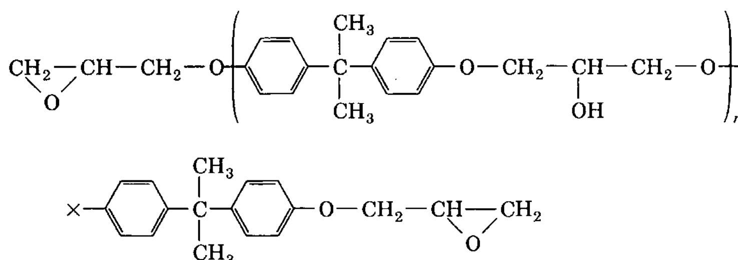
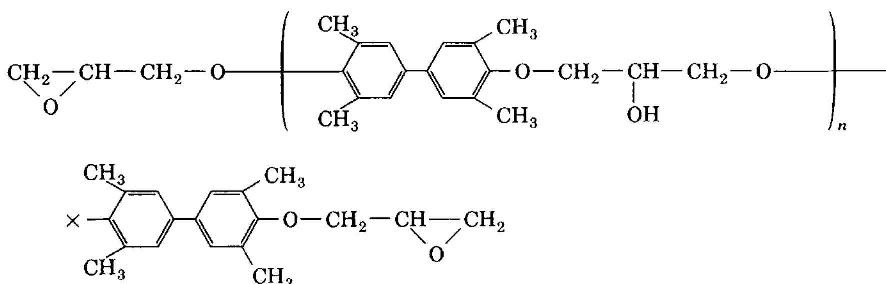
EXPERIMENTAL

Materials

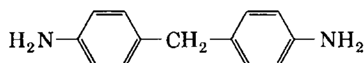
The epoxide resins used were liquid bisphenol-A type epoxide resin (DGEBA, epoxide equivalent: 190 ± 5, Epikote 828),



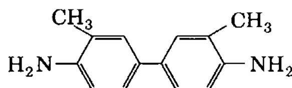
and tetramethylbiphenyl type resin (DGETMB, epoxide equivalent: ca. 180, Epikote YX-4000).



Two diamines were used as curing agents, i.e., 4,4′-diaminodiphenylmethane (DDM),



and 3,3′-dimethylbenzidine (*o*-tolidine),



Salicylic acid was used as an accelerator. These curing agents and accelerator were E.P. grade materials, and were used without further purification.

Curing of Epoxide Resins

The epoxide resins were degassed at 60°C for DGEBA and at 130°C for DGETMB under reduced pressure with stirring. Then, 1 phr of accelerator and stoichiometric amounts of curing agents were added, assuming that one epoxide group corresponds to one active hydrogen of the amino group. As the curing agents used are solid at room temperature, these agents were melted on

a hot plate and then added to the epoxide resins. The mixtures were stirred at 80°C for DGEBA and 130°C for DGETMB until the curing agents and the accelerator dissolved completely in the epoxide resins, and were then poured into molds coated with a thin film of a release agent (Frekote 44, Frekote Inc.). The DGEBA–DDM system was cured at 80°C for 2 h and then at 180°C for 6 h, and finally at 230°C for 1 h. The DGEBA–*o*-tolidine system was cured at 180°C for 6 h followed by 230°C for 1 h. Other compounds based on DGETMB were cured at 130°C for 2 h and then at 180°C for 6 h, and finally post-cured at 230°C for 1 h. In these curing conditions, the gel content and the conversion of epoxide groups for all cured samples exceeded 99 and 97%, respectively. Thus, it was confirmed that the samples are all cured to the same degree and contain scarcely any unreacted epoxide groups.

Measurements

The shapes and the dimensions of specimens for measuring the internal stress are shown in Figure 1. The steel ring on which the strain gauge (KFC-10-C-1-11, Kyowa Electric Co. Ltd.) was bonded by using adhesives was placed on the mold coated with release agent. The epoxide resin compound was cast in the space between the steel ring and the outer frame. As the cured epoxide resin is formed with the progress of curing, the steel ring is subjected to stress and raises the strain. The change of the strain δ_θ in the curing process was measured and the internal stress σ_i was calculated by using the equation[9]

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

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

In this work, the internal stress was measured only in the cooling process from 230°C to room temperature, because the internal stress of cured epoxide

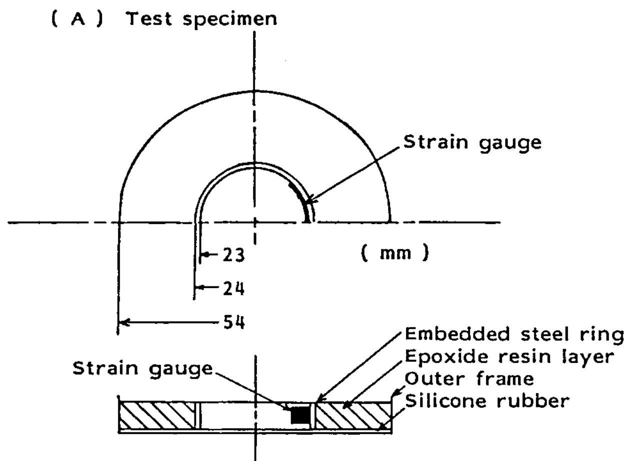


Fig. 1. Test specimen for internal stress measurement.

resins mainly occurs in the cooling process as revealed in the previous studies.[4,5]

The thermal expansion coefficient and shrinkage in the cooling process were determined from the change of sample length by using a thermomechanical analyzer (TMA CN8098F1, Rigaku Electric Co. Ltd.). The temperature range studied was from room temperature to 250°C and samples were heated at 5°C/min.

Dynamic mechanical properties were determined using an inverted free-oscillation torsion pendulum (RD-1100AD, Rhesca Co. Ltd.) according to ASTM D 2236-70.[10,11] The frequency of oscillation was adjusted to be within the range of 0.3–3.0 Hz. Samples were heated at 0.7°C/min *in vacuo*.

The average molecular weight $\overline{M}_c$(obsd) of the chain between crosslinking points were calculated from the equation for ideal rubber elasticity,[12]

$$\overline{M}_c(\text{obsd}) = \rho RT/G_r$$

where G_r and ρ are the shear modulus and the density in the rubbery region (40°C above the glass transition), respectively, R is the gas constant, and T is the absolute temperature. Though the DGETMB–*o*-tolidine system has no clear rubbery state, $\overline{M}_c$(obsd) for this system was also calculated from the shear modulus at the same temperature.

In addition, the molecular weight $\overline{M}_c$(calcd) between crosslinking points was estimated from the molecular weight of the epoxide resins and curing agent,[13] assuming that epoxide group reacted stoichiometrically with active hydrogen of the amino group.

As other experiments were carried out according to the procedure described in the previous papers,[10,14] the original sources for these techniques are only cited. The gel content of cured resins was determined by the procedure of Kenyon and Nielsen.[15] The concentration of epoxide group was measured by the method of Bell.[13]

RESULTS AND DISCUSSION

Dynamic Mechanical Properties of Cured Epoxide Resins

Dynamic mechanical properties of the bisphenol-A type and the tetramethylbiphenyl type epoxide resins cured with two types of aromatic diamines which have or do not have carbon bridge between the aromatic rings are shown in Figure 2. The T_g of the cured resins shifted to high temperature and the shear modulus in the rubbery region increased with introduction of the biphenyl structure to the epoxide resin networks. These results mean that the mobility of biphenyl unit is lower than that of bisphenol-A unit and thus the motion of the network segments is restricted with an increase in the concentration of the biphenyl segments. Moreover, we revealed in the previous paper[16] that the introduction of methyl substituents onto the aromatic rings in the bisphenol-A type resins has no effect on the T_g, the shear modulus, and the internal stress of the cured resins. Accordingly, we consider that the changes of the T_g and the shear modulus in the resin systems used in this work are not due to the presence of methyl branch on the phenylene group, but depend on the introduction of the biphenyl structure.

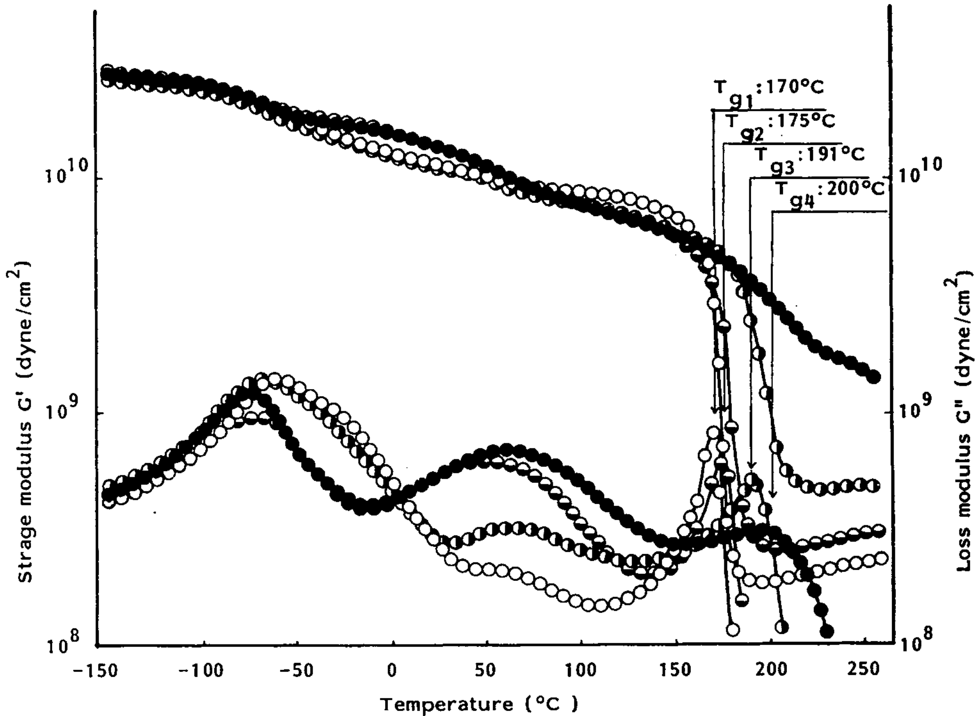


Fig. 2. Dynamic mechanical properties of cured epoxide resins. (A) Epoxide resin, DGEBA; curing agents: (○) DDM; (◒) *o*-tolidine. (B) Epoxide resin, DGETMB; curing agents: (◑) DDM; (●) *o*-tolidine. Accelerator, salicylic acid.

The glass transition temperature T_g, the molecular weight $\overline{M}_c$(obsd) and $\overline{M}_c$(calcd) between crosslinking points, and the ratio of $\overline{M}_c$(calcd) to $\overline{M}_c$(obsd) are shown in Table I. The values of $\overline{M}_c$(obsd) calculated from the theory for ideal rubber elasticity decreased with increasing the concentration of the biphenyl segments. On the other hand, the values of $\overline{M}_c$(calcd) kept nearly constant regardless of the chemical structure of the network segments. Thus, the ratio of $\overline{M}_c$(calcd) and $\overline{M}_c$(obsd) increased with introduction of the biphenyl structure to the networks. This means that the deviation from the theory of rubber elasticity increased with increasing the concentration of

TABLE I
Some Properties of Cured Epoxide Resins[a]

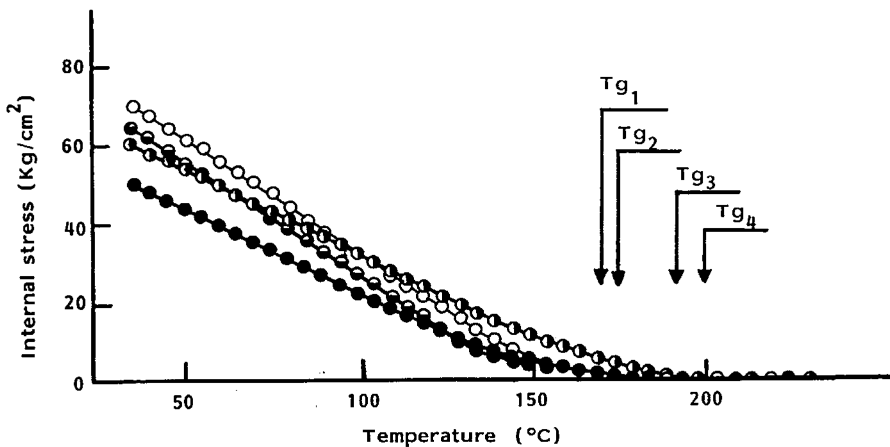
Epoxide resins	Curing agents	T_g (°C)	$\overline{M}_c$(obsd)	$\overline{M}_c$(calcd)	$\overline{M}_c$(calcd) / $\overline{M}_c$(obsd)
DGEBA	DDM	170	210	320	1.5
	o-Tolidine	175	155	320	2.1
DGETMB	DDM	191	87	310	3.7
	o-Tolidine	200	25	310	12.8

[a] T_g was determined from loss modulus G''–temp curves. Accelerator, salicylic acid.

biphenyl segments in the networks. It is well known that the theory of rubber elasticity has been derived for flexible network chain and thus is not exactly applicable for rigid network chain. Accordingly, we consider from this result that the rigidity of the epoxide resin networks was increased with the introduction of biphenyl unit, because of the low mobility of this unit.

Internal Stress in the Cured Epoxide Resins

The changes in the magnitude of the internal stress σ_i in the cooling process for four epoxide resin systems are shown in Figure 3(A). The internal stress was generated near the 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 the ambient temperature. This result is reasonable because the elastic modulus in the glassy region is almost two decades higher than that in the rubbery region.



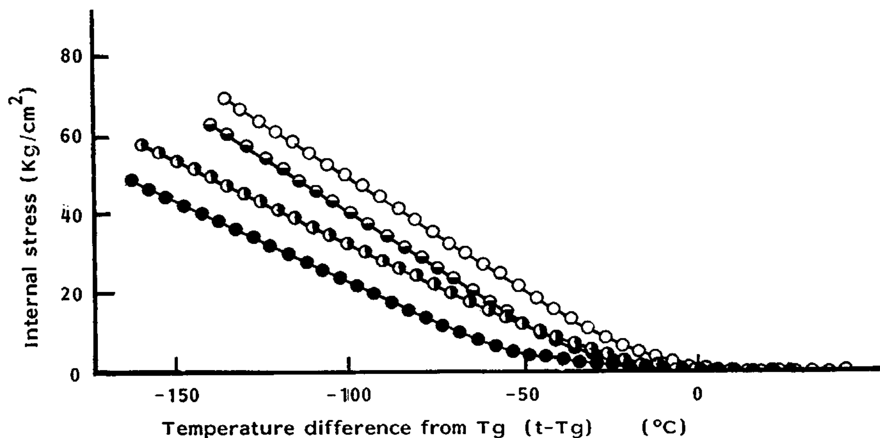


Fig. 3. Internal stresses of cured epoxide resins. Symbols as in Figure 2.

The internal stress-temperature plots constructed by regarding T_g as an original point are shown in Figure 3(B). The internal stress of these systems decreased with the increase of concentration of the biphenyl segments. In addition, it has already been shown in Figure 2 that the T_g of these systems shifts to high temperature by introducing the biphenyl structure. Thus, we conclude that the introduction of the biphenyl segment to the epoxide resin networks attains both the improvement in the heat resistance and the decrease in the internal stress of the cured epoxide resins.

Shrinkage in the Cured Epoxide Resins

The shrinkage of the cured systems in the cooling process is shown in Figure 4(A). For all cured systems, the shrinkage-temperature plots were represented by a straight line having one deflection point. The temperature where the deflection point was observed corresponds to the glass transition temperature T_g(TMA) determined by dilatometry. The values of T_g(TMA), as well as T_g by a dynamic mechanical measurement (Table I), increased with the increase in the concentration of biphenyl units. We conclude again from this result that the thermostability of the cured systems is improved by the introduction of biphenyl structure to the networks.

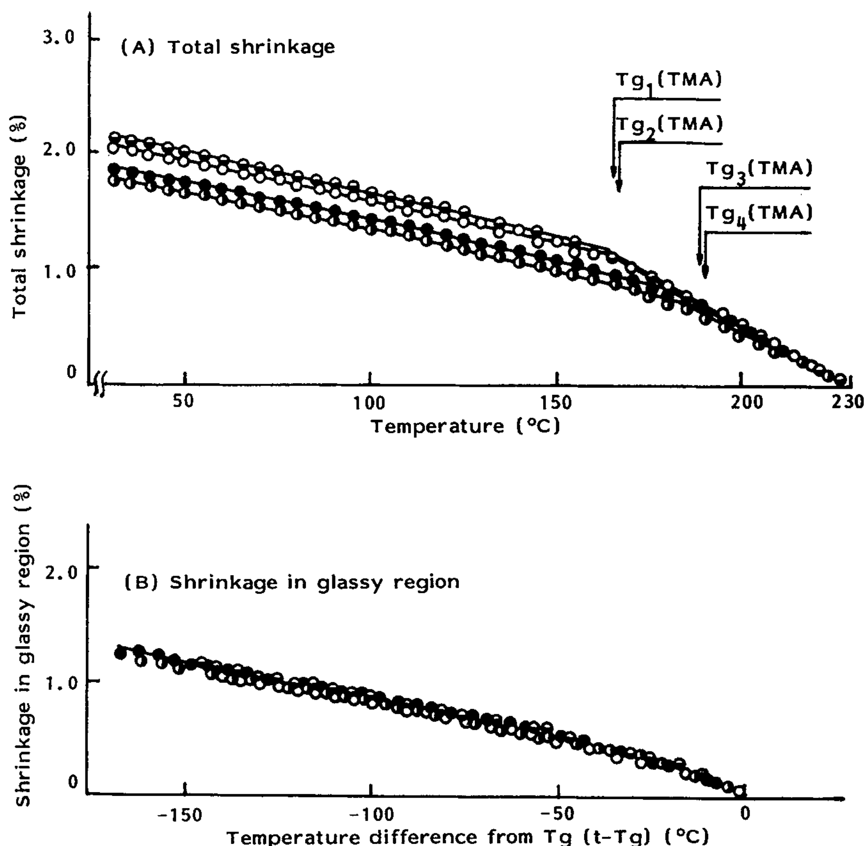


Fig. 4. Shrinkage of cured epoxide resins. Symbols as in Figure 2.

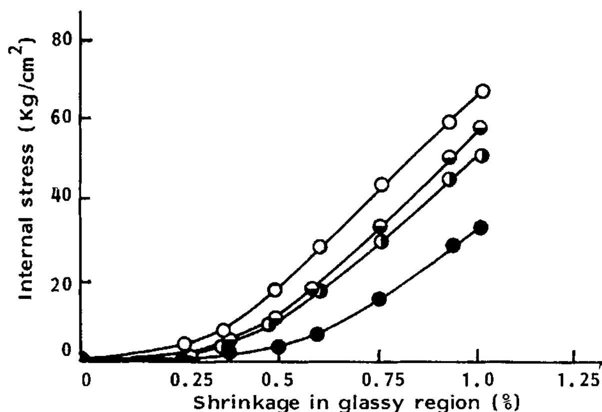


Fig. 5. Internal stress vs. shrinkage in glassy region of cured epoxide resins. Symbols as in Figure 2.

The internal stress of these systems was incurred during the cooling in the glassy ($< T_g$) region (Fig. 3). To compare with the behavior of the internal stress, the shrinkage in the same region was replotted by considering the T_g of each system as an original point and is shown in Figure 4(B). 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. This result shows that the shrinkage in the glassy region increases at a constant ratio with decrease in the ambient temperature, regardless of the chemical structure of the networks. In addition, it is clear that the linear thermal expansion coefficients α_g in the glassy region are nearly the same for all systems, because the slope of the plots of shrinkage versus temperature represents the thermal expansion coefficient.

Relationship between the internal stress and the shrinkage in the glassy region is plotted in Figure 5. The internal stress for all cured systems increased with the increasing shrinkage in the glassy region. However, the magnitude of the internal stress depended on the chemical structure of the networks and decreased with the introduction of the biphenyl segment. Accordingly, we consider that the shrinkage in the cured systems containing the biphenyl structure causes less internal stress, even if the cured resins contract at the same degree during the cooling process.

Mechanism for Reduction of Internal Stress

In order to pursue the origin for the reduction of internal stress with the introduction of biphenyl structure to the epoxide resin networks, the shear modulus of the cured resins are rewritten by regarding T_g as an original point and are shown in Figure 6. In this figure, the vertical axis is graduated with a normal section. The shear modulus in the glassy region decreased considerably with the increase of concentration of biphenyl segments in the networks. It is well known that the cured resin which has a higher modulus in the rubbery region has a lower modulus in the glassy region.[17-19] This phenomenon is explained as follows: The motion of networks is frozen in the larger free

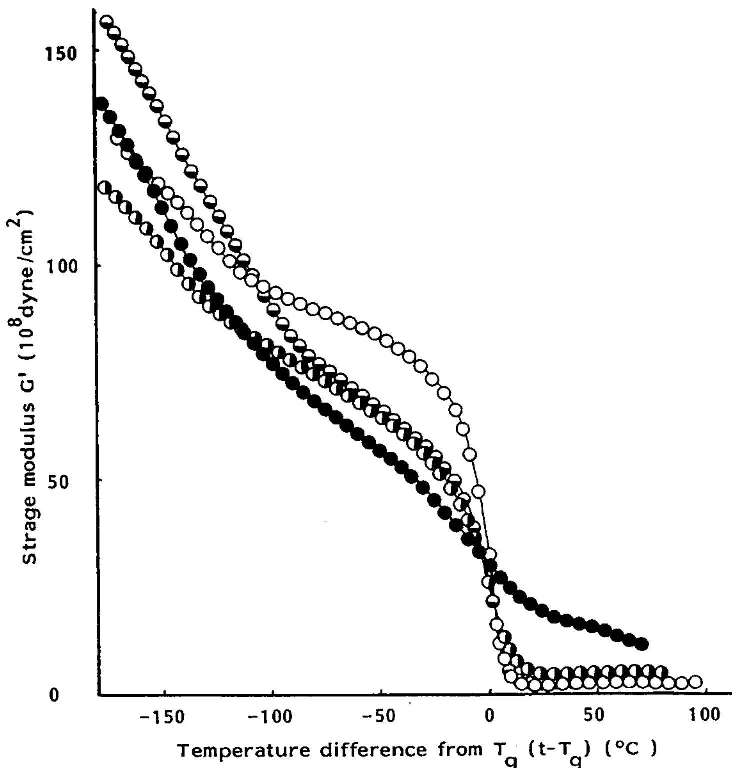


Fig. 6. Shear modulus of cured epoxide resins. Symbols as in Figure 2.

volume state with the decrease in the mobility of network segments and thus the system which has more rigid network chains has a larger free volume and a lower modulus in the glassy region.[17] As mentioned above, the mobility of the biphenyl unit is lower than that of the bisphenol-A unit. Accordingly, we consider that the reduction of the glassy modulus with the introduction of the biphenyl unit is due to the decrease in the chain mobility of the networks.

It has already been reported that the internal stress of the cured resins depends on both the shrinkage and the modulus in the glassy region.[4,5] Accordingly, we conclude that the low internal stress in the system including biphenyl segment is due to the low modulus in the glassy region of this system.

If we assume that the shrinkage in the glassy region is completely restricted by embedding a steel ring and is completely converted to the internal stress, it should be possible to calculate this stress from the thermal expansion coefficient and the Young's modulus of the cured resins.[20] If α_r is the linear expansion coefficient of the cured resins, α_s that of the steel ring, E the Young's modulus, and T the temperature, the internal stress σ_{calcd} is calculated from

$$\sigma_{\text{calcd}} = \int_{30}^{T_g} E(\alpha_r - \alpha_s)\, dT \tag{1}$$

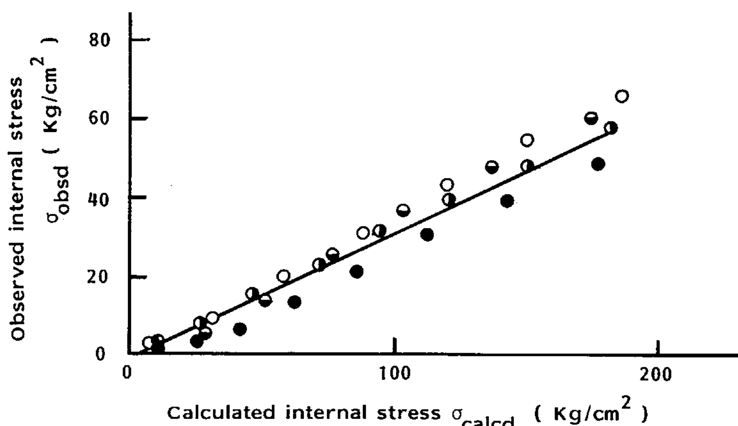


Fig. 7. Relation between observed and calculated internal stress of cured epoxide resins. Symbols as in Figure 2.

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 eq. (1) could be calculated from G by using an assumed value of 0.33 for Poisson's ratio. Accordingly, eq. (1) can be rewritten as follows:

$$\sigma_{\text{calcd}} = \int_{30}^{T_g} 2.66G(\alpha_r - \alpha_s)\, dT \qquad (2)$$

The relationship between the experimental value of σ_i and the calculated value σ_{calcd} for the cured resins is shown in Figure 7. An essentially linear relationship existed between the observed and calculated internal stresses regardless of the chemical structure of the networks. This result shows that the values of σ_i directly depend on the products of the elastic modulus and the shrinkage of the cured resins. Thus, we conclude also from this result that the reduction of the internal stress is due to the decrease of the modulus in the glassy region with the introduction of biphenyl structure.

CONCLUSION

Bisphenol-A and biphenyl type epoxide resins were cured with two types of aromatic diamines which have or do not have the carbon bridge between aromatic rings. The effect of the chemical structure of the networks on the internal stress and shrinkage of these cured systems was investigated in detail. The following conclusions were obtained:

(a) The glass transition temperature and the shear modulus in the rubbery region increased with the introduction of the biphenyl structure to the networks. These mean that the mobility of the biphenyl segment is considerably lower than that of bisphenol-A segment, and that the thermostability of the cured resins is improved with the introduction of biphenyl segment.

(b) The shear modulus in the glassy region decreased with an increase in the concentration of the biphenyl segment. This is attributed to the low mobility of the biphenyl unit. Namely, the motion of more rigid network

segment is frozen in the larger free volume state, and thus an elastic modulus in the glassy region decreases.

(c) The internal stress decreased with the introduction of the biphenyl segment. This reduction of internal stress is due to the decrease in the modulus in the glassy region, while the thermal expansion coefficient, namely, the shrinkage, remained nearly constant, even if the chemical structure of networks varied.

(d) In the previous methods for reducing the internal stress, the T_g and thus the thermostability of the cured resins were usually decreased with the reduction of the internal stress. However, it is revealed in this work that the consistency of the decrease of this stress with the increase of the heat resistance of the cured systems is possible by selecting the chemical structure of the epoxide resin and curing agent.

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