

Shrinkage and Internal Stress during Curing of Epoxide Resins

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Synopsis

The shrinkage and internal stress of bisphenol-type epoxide resins cured with aliphatic α,ω -diamines, $H_2N-(CH_2)_{m'}-NH_2$ ($m' = 2, 4, 6,$ and 12), were investigated by measuring the change of density and the strain of the steel ring embedded in the cured resins. Internal stress was found to be induced by the shrinkage occurring in the cooling process from the glass transition temperature (T_g) to room temperature. Shrinkage and internal stress increased with increase in the concentration of network chains and T_g of the cured systems, and then with a decrease in m' of the curing agents. It appears that the reductions in the concentration of network chains and T_g were necessary to reduce the shrinkage and internal stress caused by the curing.

INTRODUCTION

Epoxide resins are widely utilized in the field of coating, adhesion, lamination, and casting, etc. However, the shrinkage and the internal stress occur during the curing process, so that cracks and other defects arise in the cured resin. Therefore, it is important to know the behavior of the shrinkage and the internal stress during the curing process.

For measuring shrinkage, gravimetric and dilatometric methods^{1,2} have been applied, while bimetallic,³⁻⁷ strain-gauge,⁸⁻¹³ photoelastic,¹⁴⁻¹⁸ and other methods¹⁹⁻²⁵ have been attempted for measuring the internal stress. However, the relationship among shrinkage, internal stress, and structure of cured epoxide resins were not clarified, nor were the condition and the mechanism for the occurrence of shrinkage and internal stress.

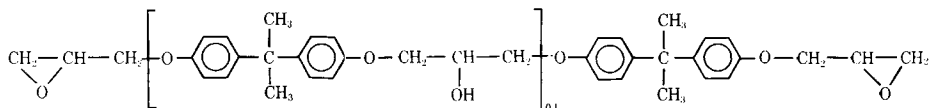
In the previous studies,²⁶⁻⁴³ we measured the mechanical, dynamic mechanical, and bonding properties and the fatigue and frictional behavior of many cured resins prepared with combinations of epoxide resins and curing agents having different chemical structures. We clarified the correlation among these properties and the relationship between the properties and the chemical structure of the epoxide resins.

In the present work, the mechanism of shrinkage and internal stress and the relationship between these properties and the chemical structure of cured epoxide resins are investigated in detail. A plan to prevent the occurrence of shrinkage and internal stress was pursued.

EXPERIMENTAL

Materials

The epoxide resin used was liquid bisphenol-type epoxide resin (epoxide equiv. 190 ± 5 ; \overline{M}_n 380; Epikote 828):



Four kinds of aliphatic α,ω -diamines, $\text{H}_2\text{N}-(\text{CH}_2)_{m'}-\text{NH}_2$, that is, ethylenediamine (EDA, $m' = 2$), tetramethylenediamine (TMDA, $m' = 4$), hexamethylenediamine (HMDA, $m' = 6$), and dodecamethylenediamine (DDMDA, $m' = 12$), were used as curing agents. These diamines were E.P.-grade materials, with purities of 97, 99, 97, and 96%, respectively, and were used without further purification.

The compositions of the epoxide resins cured with these aliphatic diamines are listed in Table I.

All the samples were cured for 4 h at 80°C and then for 4 h at 180°C . In these cases, it was confirmed that the conversion of the epoxide group could not be increased with further curing.

Measurements

Liquid epoxide resin and curing agents were mixed and degassed. The density of the liquid mixtures was measured by a pycnometer calibrated with pure water at 20°C . During and after the curing process, the density of the solid cured resins was calculated from the buoyancy of the samples in silicon oil heated to a certain temperature. Plots of temperature versus density of this silicon oil are shown in Figure 1. The change in density during heating, curing, and cooling of the epoxide resin cured with the diamines is illustrated schematically in Figure 2.⁴⁴

The sample at point A in Figure 2 is the mixture of the liquid resin and the curing agent. 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 transition temperature (T_g , point D). When the sample reaches point E, the curing cycle

TABLE I
Composition of Epoxide Resin Cured with Aliphatic Diamines^a

Curing agent ^b	phr	Conversion of epoxide group, %
Ethylenediamine	8	98
Tetramethylenediamine	12	98
Hexamethylenediamine	15	91
Dodecamethylenediamine	26	90

^a Curing condition: 80°C , 4 h/ 180°C , 4 h.

^b Curing agents were compounded stoichiometrically with the resin.

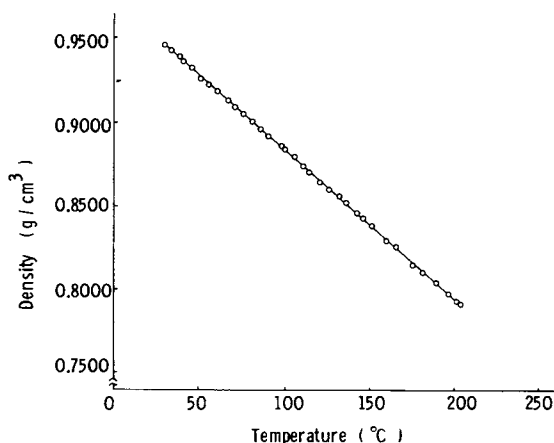


Fig. 1. Temperature vs. density of the silicon oil.

is completed. In this schematic model, the shrinkage during the curing process corresponds to B-C. On the other hand, the shrinkage during the cooling process corresponds to C-D-E. As point D shows T_g of the cured resin, the shrinkage in the glassy region ($<T_g$) corresponds to D-E, while the shrinkage at the rubbery region ($>T_g$) corresponds to C-D.

The volume contraction during the curing and cooling process was calculated from the density change of the cured system, according to the following forms⁴⁵:

Shrinkage in the rubbery region (C-D) (%):

$$\frac{\rho_{sTg} - \rho_{st}}{\rho_{l,r}} \times 100$$

Shrinkage in the glassy region (D-E) (%):

$$\frac{\rho_{sr} - \rho_{sTg}}{\rho_{l,r}} \times 100$$

Total shrinkage (A-E) (%):

$$\frac{\rho_{sr} - \rho_{lr}}{\rho_{lr}} \times 100$$

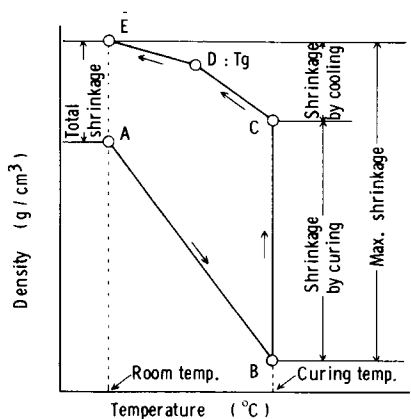


Fig. 2. Density change in curing cycle of epoxide resins.

where ρ_{lr} is the density of the mixture of the liquid (l) resin and curing agents at room temperature (r , 20°C). ρ_{st} , ρ_{sTg} , and ρ_{sr} denote the density of the solid resin at curing, at the glass transition, and at room temperatures, respectively.

The internal stress was measured by the procedure shown in Figure 3. The steel ring and the outer frame were placed on the silicon rubber. The mixtures of the epoxide resin and the curing agents were cast in the space between the steel ring and the outer frame.

The strain gauge (KFC-10-C-1-11, Kyowa Electric Co. Ltd.) was bonded to the interior side of the steel ring (thickness 0.5 mm) by using adhesives (RXE-17/DDM).

As the cured epoxide resins are formed during the progress of curing, the steel ring is subject to the stress and arise the strain.⁸⁻¹² The strain in the steel ring was measured and reduced to the internal stress by using the equation⁴⁶

$$p = Ed\delta_\theta/r$$

where P is the internal stress and E , d , r , and δ_θ are the modulus, the inside diameter, the thickness, and the strain of the steel ring, respectively.

Chemical conversion of the epoxide groups were measured by the titration.⁴⁷ Dynamic mechanical properties were measured at 0.3–3.0 Hz with a torsion pendulum according to ASTM D 2236-64T.²⁶⁻⁴³ Samples were heated at $1^\circ\text{C}/\text{min}$ in vacuo.

The concentration of the network chains (ν) was calculated from the equation of rubber elasticity.⁴⁸⁻⁵¹

$$G = \phi\nu RT$$

where G is the shear modulus at the rubbery region ($T_g + 40^\circ\text{C}$), ϕ is the front factor, which is unity for ideal rubbers, R is the gas constant, and T is the absolute temperature. The parameter ν is the number of moles of network chains per unit volume, that is, the so-called density of crosslinks in the cured resins.⁵¹

Thermal expansion coefficients were calculated from the slope of the plots of density versus temperature:

$$\beta = \frac{\rho_{t_1} - \rho_{t_2}}{\rho_{t_2} (t_2 - t_1)}$$

where β is the thermal expansion coefficient, ρ_{t_1} and ρ_{t_2} are the density of the cured resin at temperature t_1 and room temperature t_2 , respectively.

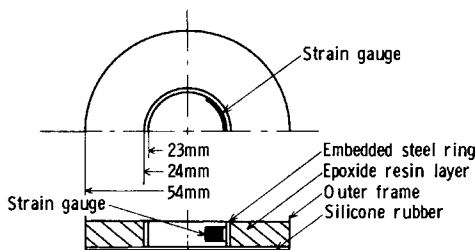


Fig. 3. Two-dimensional casting model for strain gauge method.

RESULTS AND DISCUSSION

Physical Properties in the Cured Epoxy Resins

Dynamic mechanical properties of the bisphenol-type epoxy resin cured with four kinds of aliphatic diamines of different numbers of methylene linkages are shown in Figure 4. Since the measurements were carried out under 0.3–3.0 Hz, the temperature where the elastic modulus decreased drastically and the damping showed the maximum value was regarded as the glass transition temperature (T_g).

The T_g of the cured resins and the elastic modulus at the glassy ($<T_g$) and rubbery ($>T_g$) regions increased with decrease in m' of the curing agents.

The concentration of the network chains (ν) was calculated from the equation of rubber elasticity,⁴⁸ and the plots of ν vs. m' are shown in Figure 5. An approximately linear relationship existed between ν and m' . From this result, it can be seen that the concentration of network chains in the cured resins was governed by the number of methylene linkage in the curing agents.

The plots of ν vs. T_g of the cured systems are shown in Figure 6; there is a linear relationship. It is apparent that the motion of the network segments is restricted at high temperatures with an increase in ν of the cured resins. Namely, the glass transition temperature of the cured resins was governed by the concentration of network chains.

Plots of the thermal expansion coefficient β vs. temperature are shown in Figure 7. The value of β changed remarkably in the T_g region, while it remained unchanged in the glassy ($<T_g$) and in the rubbery ($>T_g$) region. The β values in the glassy and rubbery regions did not depend on m' .

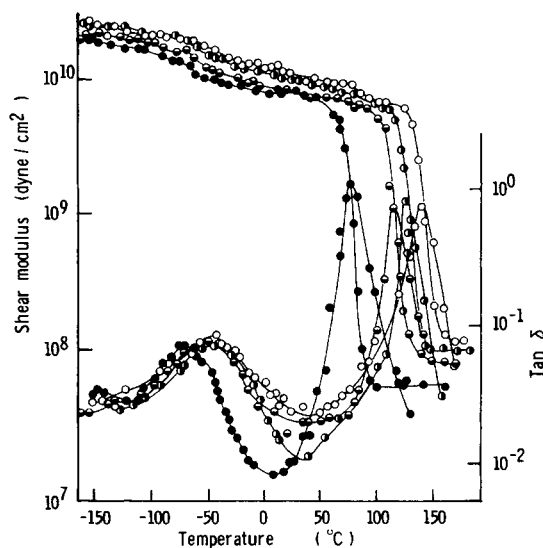


Fig. 4. Dynamic mechanical properties of cured epoxy resins. Curing agents: (O) ethylenediamine ($m' = 2$); (●) tetramethylenediamine ($m' = 4$); (◐) hexamethylenediamine ($m' = 6$); (◑) dodecamethylenediamine ($m' = 12$). Epoxy resin: bisphenol A DGE (Epikote 828).

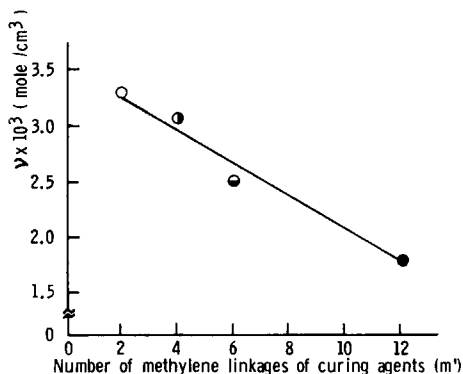


Fig. 5. Concentration of network chains vs. m' of cured epoxide resins. Curing agents: (○) ethylenediamine ($m' = 2$); (●) tetramethylenediamine ($m' = 4$); (◐) hexamethylenediamine ($m' = 6$); (●) dodecamethylenediamine ($m' = 12$). Epoxide resin: bisphenol A DGE (Epikote 828).

Shrinkage in the Cured Epoxide Resins

The relationship of the shrinkage in each step of the curing cycle shown in Figure 1 to the T_g of the cured epoxide resins is shown in Table II. With increase in m' of the curing agents, T_g and the shrinkage in the glassy region (D-E) decreased, while the shrinkage in the rubbery region (C-D) increased.

The plots of the shrinkage in the rubbery region (C-D) vs. temperature are shown in Figure 8. The shrinkage in the rubbery region increased linearly with decrease in temperature. Contraction at a constant ratio from the curing temperature (180°C) to the glass transition temperature is natural because the thermal expansion coefficient was kept constant in these temperature region.

The plots of shrinkage in the glassy region vs. temperature are shown in Figure 9. As the glass transition temperatures of these cured systems are different from each other (T_{g2} 135°C, T_{g4} 126°C, T_{g6} 110°C, and T_{g12} 75°C), the shrinkage in the glassy region arises at different temperatures, that is, at the T_g of each system (T_{g2} , T_{g4} , T_{g6} , T_{g12}). In this figure, the dependences of shrinkage on the temperature were nearly constant in all systems.

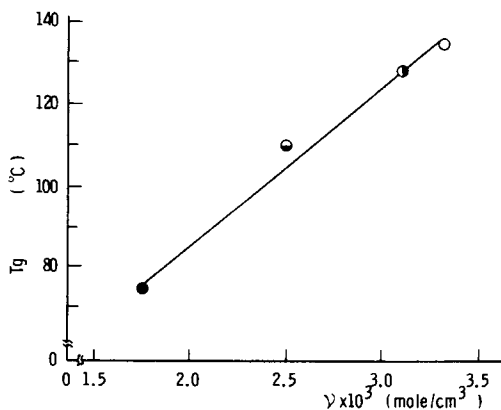


Fig. 6. T_g vs. concentration of network chains of cured epoxide resins. Curing agents: (○) ethylenediamine ($m' = 2$); (●) tetramethylenediamine ($m' = 4$); (◐) hexamethylenediamine ($m' = 6$); (●) dodecamethylenediamine ($m' = 12$). Epoxide resin: bisphenol A DGE (Epikote 828).

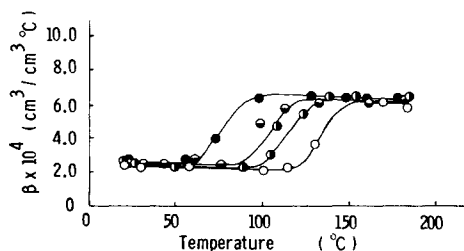


Fig. 7. Coefficient of thermal expansion of cured epoxy resins vs. temperature. Curing agents: (○) ethylenediamine ($m' = 2$); (◐) tetramethylenediamine ($m' = 4$); (◑) hexamethylenediamine ($m' = 6$); (●) dodecamethylenediamine ($m' = 12$). Epoxide resin: bisphenol A DGE (Epikote 828).

To compare the behavior of shrinkage in these systems, the shrinkage-temperature plots, rewritten by considering the T_g of the each system as an original point, are shown in Figure 10. 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, even if m' and ν are different in each system. It was concluded 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 curing agent.

The plots of the shrinkage in the glassy region vs. the concentration of network chains are shown in Figure 11. An approximately linear relationship existed between ν and the shrinkage in the glassy region. Namely, as a general rule, the shrinkages in the glassy region were governed by the concentration of the network chains.

Internal Stress in the Cured Epoxy Resin

Internal stress, β , ν , and T_g of the epoxy resins cured with diamines having the different number of methylene linkages are shown in Table III. ν and T_g of the cured resins increased with decrease in m' of the curing agents, while the values of β were roughly constant in the glassy and in the rubbery region, even if m' changed from 2 to 12. The internal stress at ordinary temperature (25°C) increased with increase in ν and T_g of the cured resins. Accordingly, it is assumed that the internal stress must be related to the concentration of the network chains and the glass transition temperature of the cured resins.

TABLE II
Relationship between the Shrinkages and T_g of Cured Epoxy Resins^a

Curing agents	Total shrinkage A-E (%)	Max. shrinkage B-E (%)	Shrinkage by cooling (%)			T_g (°C)
			From curing temp. to room temp. C-E	From curing temp. to T_g C-D	From T_g to room temp. D-E	
Ethylenediamine	5.1	10.5	5.9	2.9	3.0	135
Tetramethylenediamine	4.8	10.1	6.9	4.1	2.8	126
Hexamethylenediamine	6.5	9.8	7.4	4.9	2.5	110
Dodecamethylenediamine	7.0	8.5	8.4	6.8	1.6	75

^a Epoxide resin: Bisphenol A DGE (Epikote 828). Curing condition: 80°C, 4 h/180°C, 4 h.

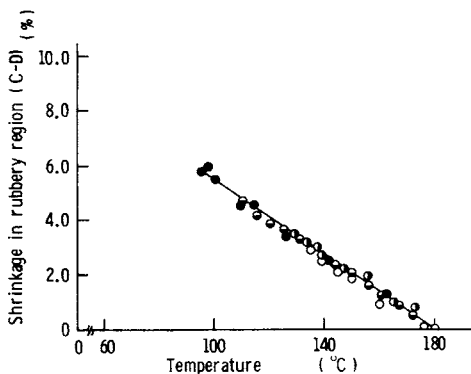


Fig. 8. Shrinkage in rubbery region vs. temperature of cured epoxide resins. Curing agents: (○) ethylenediamine ($m' = 2$); (◐) tetramethylenediamine ($m' = 4$); (◑) hexamethylenediamine ($m' = 6$); (●) dodecamethylenediamine ($m' = 12$). Epoxide resin: bisphenol A DGE (Epikote 828).

The changes in the magnitude of the internal stress during the cooling process are shown in Figure 12. The internal stresses were changed dramatically at T_g of each cured resins (T_{g2} , T_{g4} , T_{g6} , and T_{g12}). Internal stresses were almost absent in the rubbery ($>T_g$) region. However, they increased greatly with decreasing ambient temperature in the glassy ($<T_g$) region.

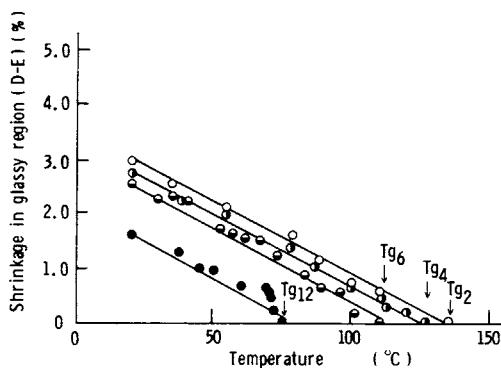


Fig. 9. Shrinkage in glassy region of cured epoxide resins vs. temperature. Curing agents: (○) ethylenediamine ($m' = 2$); (◐) tetramethylenediamine ($m' = 4$); (◑) hexamethylenediamine ($m' = 6$); (●) dodecamethylenediamine ($m' = 12$). Epoxide resin: bisphenol A DGE (Epikote 828).

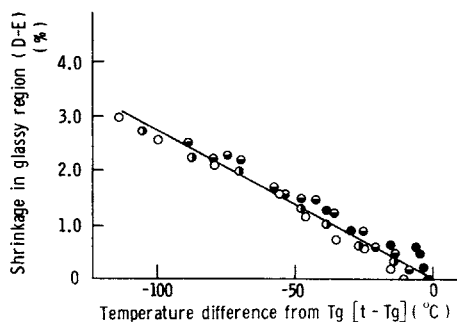


Fig. 10. Shrinkage in glassy region vs. $t - T_g$ of cured epoxide resins. Curing agents: (○) ethylenediamine ($m' = 2$); (◐) tetramethylenediamine ($m' = 4$); (◑) hexamethylenediamine ($m' = 6$); (●) dodecamethylenediamine ($m' = 12$). Epoxide resin: bisphenol A DGE (Epikote 828).

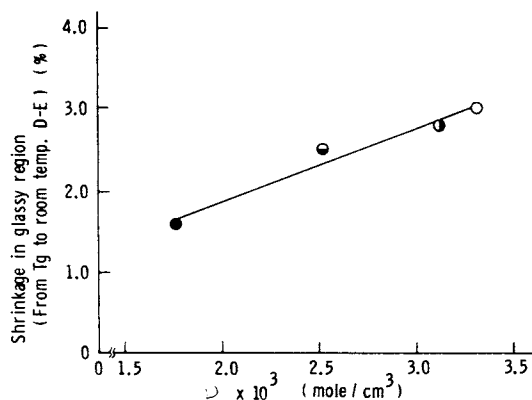


Fig. 11. Shrinkage in glassy region vs. concentration of network chains of cured epoxide resins. Curing agents: (O) ethylenediamine ($m' = 2$); (●) tetramethylenediamine ($m' = 4$); (◐) hexamethylenediamine ($m' = 6$); (●) dodecamethylenediamine ($m' = 12$). Epoxide resin: bisphenol A DGE (Epikote 828).

The internal stress–temperature plots constructed by regarding T_g as original point are shown in Figure 13. From these plots, the changes in the internal stress appeared to be represented by a straight line, even though m' of the curing agents varied from 2 to 12. The magnitude of the shrinkage and internal stress in the glassy region depended on the temperature difference from T_g , as shown in Figures 10 and 13, respectively.

Thus, the relationship of the internal stresses to the shrinkages in the glassy region is plotted in Figure 14. An approximately linear relationship existed between the shrinkage and the internal stress in the glassy region, except near T_g . From this result, we conclude that the shrinkages in the glassy region were converted directly to internal stress, because the motion of the network segments was restricted in this region. On the other hand, large internal stress could not be generated in the rubbery region, as shown in Figure 11, for reason that the motion of the network segments was easy and the cured system had a large relaxational ability in this region.

A mineral filler having a small expansion coefficient was used to be loaded the epoxide resins to reduce the shrinkage and internal stress. This was an example to show that the internal stress can be reduced by decreasing the shrinkage in the glassy region.

TABLE III
Internal Stress, β , ν and T_g of Cured Epoxide Resins^a

Curing agents	Internal stress (25°C) (kg/cm ²)	Coefficient of thermal expansion $\beta \times 10^4$ (cm ³ /cm ³ °C)		T_g (°C)	Concentration of network chains $\nu \times 10^3$ (mol/cm ³)
		Glassy region	Rubbery region		
Ethylenediamine	66	2.60	6.60	135	3.30
Tetramethylenediamine	52	2.60	6.91	126	3.10
Hexamethylenediamine	45	2.72	6.07	110	2.50
Dodecamethylenediamine	30	2.81	6.52	75	1.75

^a Epoxide resin: Bisphenol A DGE (Epikote 828). Curing condition: 80°C, 4 h/180°C, 4 h.

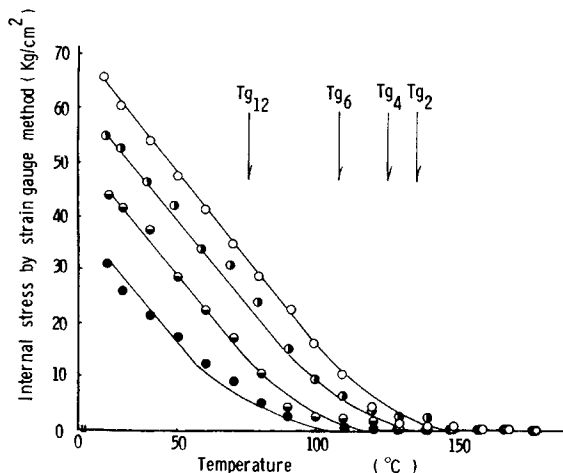


Fig. 12. Internal stress of cured epoxide resins vs. temperature. Curing agents: (○) ethylenediamine ($m' = 2$); (◐) tetramethylenediamine ($m' = 4$); (◑) hexamethylenediamine ($m' = 6$); (●) dodecamethylenediamine ($m' = 12$). Epoxide resin: bisphenol A DGE (Epikote 828).

Plots of internal stress vs. v of the cured resins are shown in Figure 15. An approximately linear relationship existed between the internal stress vs. v . This result means that the internal stress of these systems depended upon the concentration of network chains. Therefore, we propose that the concentration of network chains be decreased in order to reduce the internal stress. This general rule may be applied to the systems cured with acids besides amines shown in the present article. From this standpoint, the internal stress is expected to decrease with increase in the chain length of the epoxide resins.

CONCLUSIONS

Bisphenol-type epoxide resins were cured with four kinds of aliphatic α,ω -diamines, and the magnitudes of the internal stress and the shrinkage were

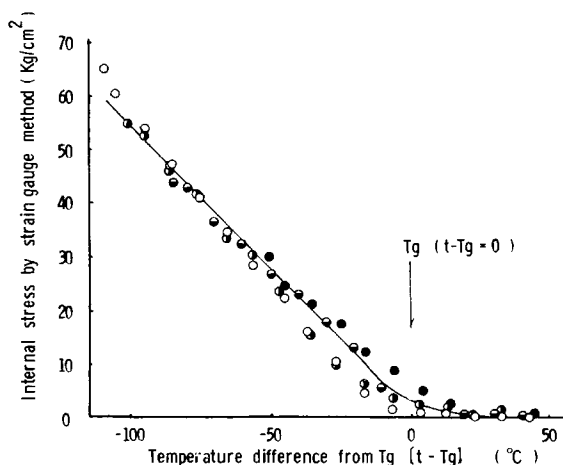


Fig. 13. Internal stress vs. $t - T_g$ of cured epoxide resins. Curing agents: (○) ethylenediamine ($m' = 2$); (◐) tetramethylenediamine ($m' = 4$); (◑) hexamethylenediamine ($m' = 6$); (●) dodecamethylenediamine ($m' = 12$). Epoxide resin: bisphenol A DGE (Epikote 828).

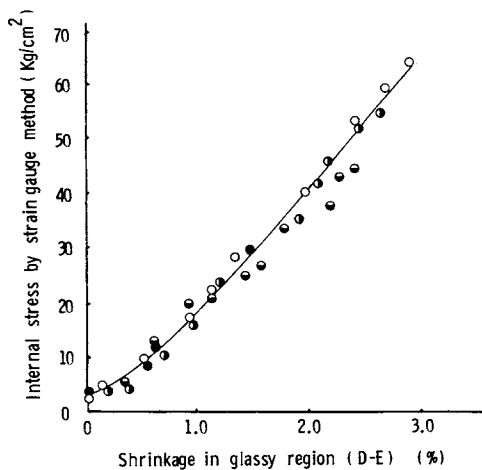


Fig. 14. Internal stress vs. shrinkage of cured epoxy resins in glassy region. Curing agents: (O) ethylenediamine ($m' = 2$); (◐) tetramethylenediamine ($m' = 4$); (◑) hexamethylenediamine ($m' = 6$); (●) dodecamethylenediamine ($m' = 12$). Epoxide resin: bisphenol A DGE (Epikote 828).

related to the chemical structure of the cured resins.

The following conclusions were obtained:

(1) The internal stresses in these cured systems are mainly induced by shrinkages in the glassy region.

(2) A linear relationship exists between the internal stress and the concentration of network chains, the shrinkage in the glassy region, or the temperature differences from T_g to room temperature.

(3) The concentration of network chains and the glass transition temperature of the cured resins are linearly increased with decrease in the number of methylene linkages, so that the temperature difference between the glass transition temperature and the room temperature ($t - T_g$) is decreased. Therefore, the shrinkage and the internal stress in the glassy region are increased with increase in $t - T_g$, since the thermal expansion coefficient is kept constant in spite of the

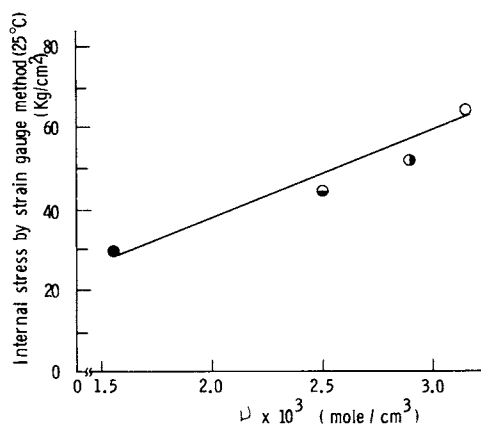


Fig. 15. Internal stress vs. concentration of network chains of cured epoxy resins. Curing agent: (O) ethylenediamine ($m' = 2$); (◐) tetramethylenediamine ($m' = 4$); (◑) hexamethylenediamine ($m' = 6$); (●) dodecamethylenediamine ($m' = 12$). Epoxide resin: bisphenol A DGE (Epikote 828).

kind of curing agent used.

(4) In general, the internal stress is reduced by increasing the chain length between the functional groups of the curing agents or by decreasing the concentration of the network chains.

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