

The Mechanism for Occurrence of Internal Stress during Curing Epoxide Resins

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SYNOPSIS

The mechanism for the occurrence of internal stress in the curing cycle of four-functional epoxide resins was investigated in detail. The internal stress in this system was generated at the vitrification point in the course of curing, because the modulus of samples was rapidly increased at this point. After the vitrification point, the internal stress was increased with an increase of the shrinkage in the curing and cooling processes.

Moreover, the magnitude of the internal stress in the four-functional resin systems depended on the chemical structure of aromatic diamines used as curing agents. This was explained by the difference of curing shrinkage after vitrification in each system.

INTRODUCTION

Epoxide resins are widely utilized as encapsulating materials, laminates, and adhesives in the fields of electric and electronic industries. However, epoxide resins usually shrink during the curing and cooling processes. If the shrinkage is constrained by an adhesion with other materials, the constrained shrinkage is converted to internal stress.¹⁻⁵ The internal stress causes various defects, such as crack, delamination, and void. Therefore, it is of great importance to prevent or reduce shrinkage and internal stress of cured epoxide resins.

In previous studies,⁶⁻¹⁰ we cleared the mechanism for the occurrence of internal stress in two-functional resin systems, of which the glass transition temperature (T_g) was lower than the curing temperature. The cured resins were in the rubbery state when the curing reaction was completed. Thus, in-

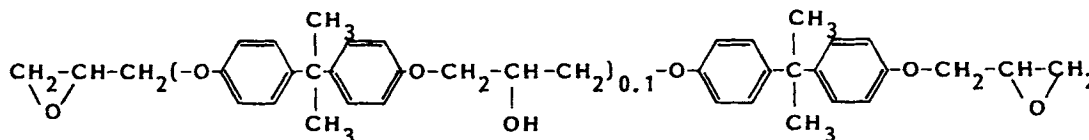
ternal stress in these systems was not observed in the curing process and occurred mainly in the cooling process from T_g to room temperature. The magnitude of this stress depended on both the elastic modulus and the thermal expansion coefficient in the glassy region of the cured resins.¹¹⁻¹³

In the present work, the mechanism for the occurrence of internal stress in four-functional resin systems that have higher T_g is investigated in detail. In addition, the effect of the chemical structure of curing agents on the internal stress is pursued.

EXPERIMENTAL

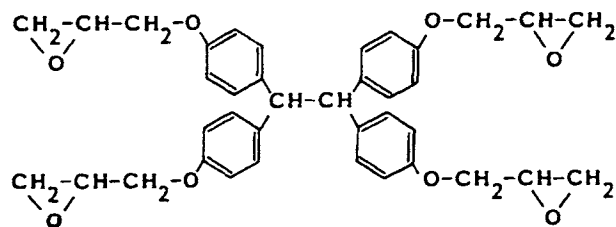
Materials

The two-functional epoxide resin used was bisphenol-A type resin (DGEBA, epoxide equivalent: 190 ± 5 , Epikote 828):

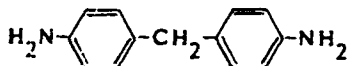


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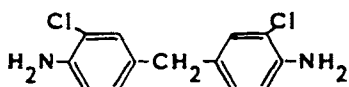
and the four-functional resin used was 1,1,2,2-tetra-phenylglycidyletherethane (TPGEE, epoxide equivalent: ca. 198, Epikote 1031s):



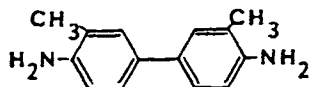
Four kinds of aromatic diamines were used as curing agents, i.e., 4,4'-diaminodiphenylmethane (DDM):



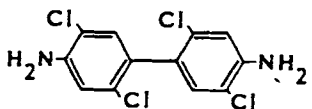
3,3'-dichloro-4,4'-diaminodiphenylmethane (Cl-DDM):



3,3'-dimethyl-4,4'-diaminobiphenyl (DMB):



and 2,2',-5,5'-tetrachloro-4,4'-diaminobiphenyl (TCB):



These curing agents were E.P. grade materials and were used without further purification.

Curing of Epoxide Resins

Epoxide resins were degassed at 80°C for DGEBA and at 180°C for TPGEE under reduced pressure. Curing agents were also degassed at 150°C under reduced pressure. These epoxide resins and curing agents were kept at 180°C in the draft oven for 20 min. Then, stoichiometric amounts of the curing agents were mixed in the epoxide resins, assuming that one epoxide group corresponds to one active hydrogen of the amino group. The mixtures were stirred until the curing agents were completely dissolved in the epoxide resins and were then poured into molds. All resin systems were cured at 200°C for 4 h.

Measurements

Internal stress was measured by the procedure shown in Figure 1. The steel ring bonded by a strain gauge (KFC-10-C-1-11, Kyowa Electric Co. Ltd.) is placed in the silicone rubber mold. The mixtures of epoxide resin and curing agents are cast in the space between the steel ring and the outer frame. As the cured epoxide resins are formed during the progress of curing, the steel ring is subject to the stress and increases the strain. The strain δ_θ of the steel ring is measured during both curing and cooling processes. To cancel the thermal expansion of the ring, the thermal strain δ_t of the steel ring is subtracted from the value of δ_θ . Internal stress σ_i is calculated by using the equation¹⁴

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

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

The change in density during curing cycle of two-functional epoxide resin systems is illustrated schematically in Scheme 1. The sample at point A is mixture of resin and curing agent at room temperature. The sample is heated to the curing temperature (200°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 D) through the T_g (point E). The curing cycle is completed at point D. In this schematic model, the curing shrinkage corresponds to B–C. On the other hand, the cooling shrinkage corresponds to C–E–D. As point E shows the T_g of the cured resin, the shrinkage in the glassy region ($< T_g$) corresponds to E–

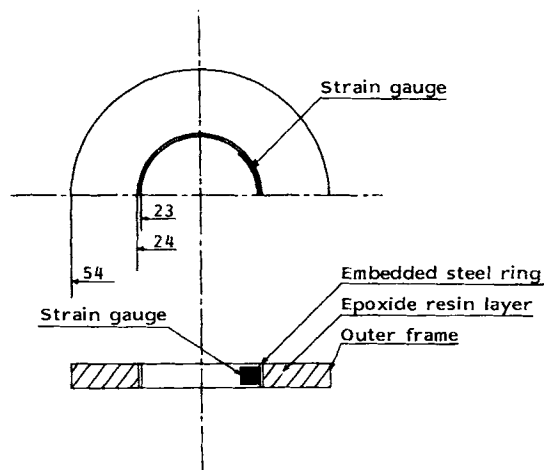
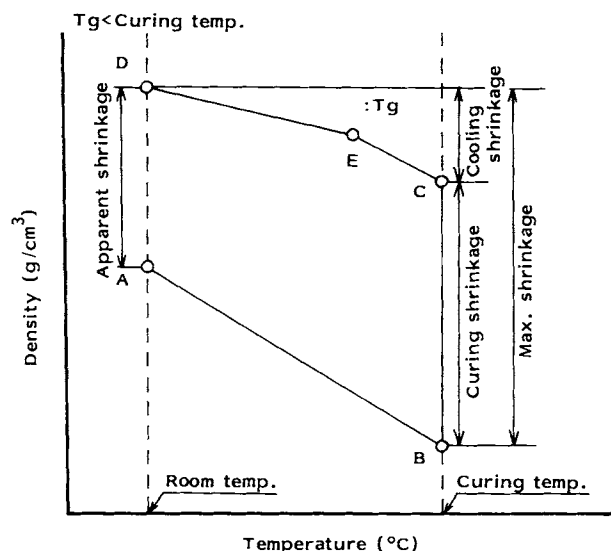


Figure 1 Test specimen for the internal stress measurement.



Scheme 1 Density change in curing cycle of epoxide resins.

D, whereas the shrinkage at the rubbery region ($> T_g$) corresponds to C-E.

The change in density during the curing process was calculated from the change of buoyancy in silicone oil at the curing temperature (200°C). The density were converted to shrinkage by using following equations:

Curing shrinkage

$$= (1/\rho_0 - 1/\rho_t)/1/\rho_0 \times 100 (\%)$$

where ρ_0 and ρ_t are the density of uncured samples and the density at curing time t , respectively. The density change in the cooling process was calculated from the change of sample length, which was measured by using a thermomechanical analyzer (TMA CN8098F1, Rigaku Electric Co.). Samples were heated at $5^\circ\text{C}/\text{min}$:

$$\rho_T = \rho_{200} / \{1 + 3\alpha(T - 200)\}$$

where ρ_{200} and ρ_T are the density of cured sample at 200°C (curing temperature) and at sample temperature T , respectively. α is the linear thermal expansion coefficient measured by TMA.

Dynamic mechanical properties were determined using an inverted free oscillation torsion pendulum (RD-1100AD, Rhesca Co.) according to ASTM D-2236-70.^{15,16} The frequency of oscillation was adjusted within the range of 0.1–2.0 Hz. Samples were heated at $0.7^\circ\text{C}/\text{min}$ *in vacuo*.

The chemical conversion of epoxide groups was

determined by the change in the absorbance ratio of epoxide (915 cm^{-1}) to phenylene groups (1600 cm^{-1}) in the IR spectra of cured resins.

The vitrification point was determined by indentation measurement. A flat-ended rod with diameter 1.0 mm was used as an indentation probe. A constant load (400 g) was applied to the probe, and the displacement of the probe was recorded as a function of curing time. When the displacement began to approach the constant value, the curing time was regarded as the vitrification point.

RESULTS AND DISCUSSION

Internal Stress Occurring in the Curing Process

The change in the internal stress during curing and cooling processes for two- and four-functional epoxide resins (DGEBA and TPGE) are shown in Figure 2. The internal stress of two-functional resin system was not generated in the curing process (B–C), but increased greatly with decreasing temperature in the cooling process (C–D). The T_g of this system was 165°C and was lower than the curing temperature (200°C); i.e., this system was in a rubbery state at the curing temperature even after completion of curing. Therefore, the shrinkage in the curing process (B–C) is not converted to the internal stress. On the other hand, the internal stress of the four-functional resin system occurred in both the curing and cooling processes. As T_g of this system was 308°C and was higher than the curing temperature, the cured resin was vitrified in the course of the curing process. The vitrification point in this system is about 1 min, as shown in Table I. Accordingly, the internal stress of this system seemed to be generated at the vitrification point (X) and increased with an increase in shrinkage after point X. This is reasonable because the modulus of the sample increases greatly at this point, as shown in Figure 3.

The internal stress at room temperature (point D) in the four-functional resin system is about two times higher than that in the two-functional resin system. This result showed that for decreasing the internal stress of the former system it is important to reduce the internal stress during the curing process.

Effect of the Chemical Structure of Curing Agents on the Internal Stress in the Curing Process

The chemical conversion of epoxide groups, glass transition temperature (T_g), and vitrification point

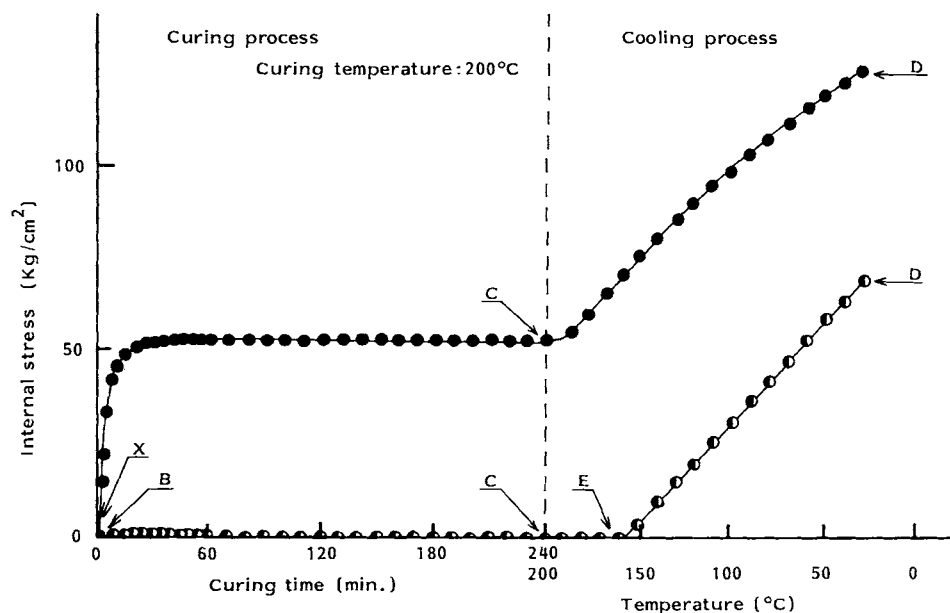


Figure 2 Internal stress during the curing and cooling processes for epoxide resins. Epoxide resins: (●) DGEBA (Epikote 828, T_g 165°C); (●) TPGE (Epikote 1031s, T_g 308°C); curing agent: DDM.

of the four-functional epoxide resins cured with four aromatic diamines are summarized in Table I. In all samples, the conversion of epoxide groups was more than 94% and the glass transition temperature was above 300°C. Thus, it was confirmed that all samples contain scarcely any unreacted epoxide groups and vitrify in the course of the curing process. The vitrification time of the cured resins shifted to a longer time with the introduction of a larger substituent group on aromatic rings of the curing agents. This result can be interpreted as the result of the delay of curing rate with the steric hindrance by the large substituents.

The internal stress of these systems in the curing process are shown Figure 4. In all systems, the internal stress occurred at the vitrification point and

attained constant values when the curing reaction was completed. However, the constant values of internal stress decreased with the introduction of a larger substituent group in the following order: DDM > DMB > Cl-DDM > TCB. These results show that the internal stress could be decreased by selecting the chemical structure of curing agents with no reduction of the heat resistance of the cured resins.

Shrinkage in Curing Process

The shrinkage in the curing process of the four cured systems are shown in Figure 5(A). In all systems, the volume of sample transitionally increased at the beginning of curing. Then, the sample rapidly

Table I Some Properties of Epoxide Resin Curing Systems

Curing Agents	Chemical Conversion of Epoxide Groups (%)	Glass Transition Temperature (°C)	Vitrification Point (min)	Internal Stress During Curing Process (kg/cm ²)
DDM	95	308	1	52
DMB	94	309	2	40
Cl-DDM	98	304	8	20
TCB	96	306	33	7

Epoxide resin: TPGE (Epikote 1031s).

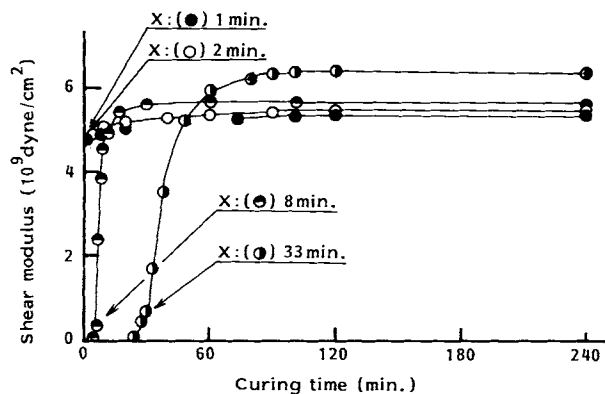


Figure 3 Shear modulus in the curing process for the epoxide resins. Epoxide resin: TPGEE (Epikote 1031s); curing agents: (●) DDM, (○) DMB, (◐) Cl-DDM, (◑) TCB.

shrunk with the progress of curing and attained the constant values when curing reaction was completed. We supposed that this expansion of sample is due to the rise of sample temperature with the exothermic reaction. Indeed, the sample temperature increases rapidly at the initial stage of curing reaction (Fig. 6).

As the internal stress in these systems occurred at the vitrification point, shrinkage after this point is observed [Fig. 5(B)]. The magnitude of the shrinkage after vitrification is sensitively affected by the structure of curing agents and reduced with introducing larger substituent groups in the curing agents (DDM > DMB > Cl-DDM > TCB). The mechanism for this reduction will be discussed in a later section. The order of the reduction in the shrinkage is in good agreement with that of the in-

ternal stress. The relationship between internal stress and shrinkage after the vitrification point is plotted in Figure 7. Internal stress for all cured systems increased linearly with increasing shrinkage after vitrification, regardless of the chemical structure of the curing agents. Accordingly, we conclude that the reduction of internal stress with the introduction of substituents in the curing agents is attributed to the decrease of the shrinkage after vitrification.

Mechanism for Reduction of Internal Stress and Shrinkage

The temperature of samples during curing reaction is shown in Figure 6. The sample temperature in all systems rose at the initial stage of curing and showed the peak at some curing time. This is natural because the curing reaction of these systems is an exothermic reaction. In addition, the peak temperature reduced with the introduction of the larger substituent group. This result is also reasonable because the rate of curing reaction decreases with the introduction of the larger substituent.

It is expected that the increase of sample temperature at the initial stage of curing should affect the sample volume in the curing process. Thus, the density of the Cl-DDM cured system is plotted against the sample temperature in Figure 8. The sample did not monotonously shrink in the curing process (B-C). The sample was first expanded with an increase in the sample temperature and then shrunk rapidly with a decrease in the temperature. Thus, it is clear that the shrinkage in the curing process is the sum of the curing shrinkage with the

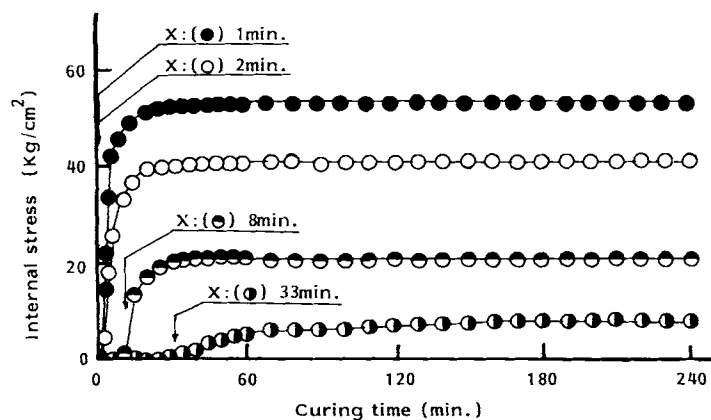


Figure 4 Internal stress in the curing process for the epoxide resins cured with aromatic diamines. Symbols the same as in Figure 3.

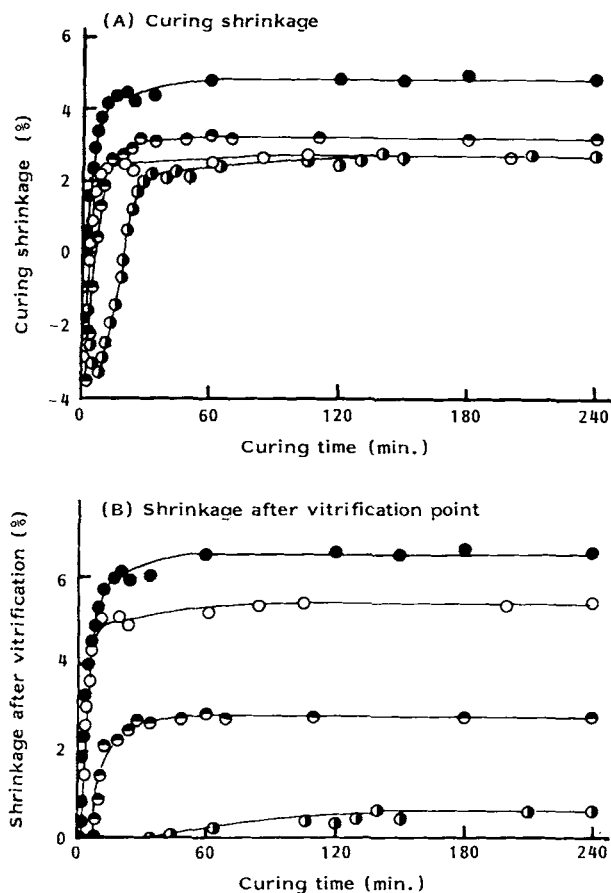


Figure 5 Shrinkage in the curing process for the epoxide resins. Symbols as in Figure 3.

progress of the curing reaction and the cooling shrinkage with cooling from peak temperature to curing temperature. The cooling shrinkage after

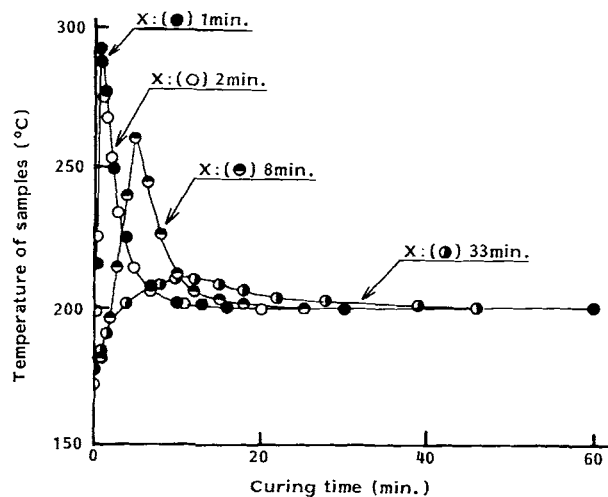


Figure 6 Sample temperature in the curing process for the epoxide resins. Symbols as in Figure 3.

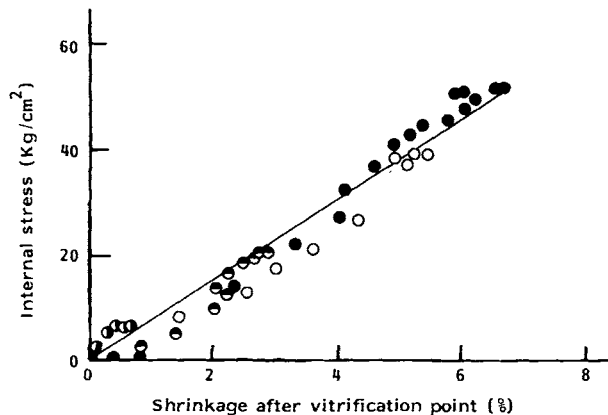


Figure 7 Internal stress vs. shrinkage after vitrification point for the epoxide resins. Symbols as in Figure 3.

vitrification in this process should decrease with the introduction of the larger substituent, because the sample temperature at the vitrification point decreases, as shown in Figure 6. Accordingly, we conclude that the reduction of the curing shrinkage after vitrification is due to the decrease of the cooling shrinkage in this region.

As reported in previous papers,¹¹⁻¹³ internal stress is affected not only by shrinkage, but also by the modulus in the glassy region. The changes of modulus in the curing process are shown in Figure 3. In all systems, the modulus increases rapidly from the vitrification point and attains nearly constant values with the completion of curing.

If we assume that the shrinkage after the vitrification point is completely restricted by embedding a steel ring and is converted to the internal stress, it should be possible to calculate this stress as the

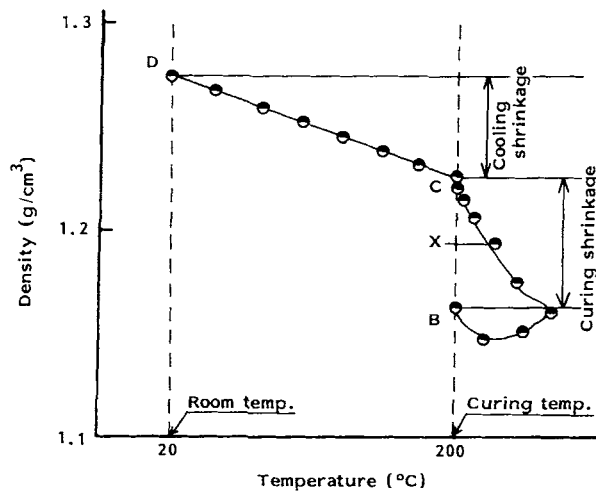


Figure 8 Density change in curing cycle of Cl-DDM cured system.

product of the strain ϵ and the Young's modulus E after the vitrification point. However, the value of ϵ and E change with the progress of curing. Thus, if γ is the time coefficient of the strain, i.e., the slope of the shrinkage-curing time curves shown in Figure 5(B); t , the curing time; and t_{vp} , the vitrification time; the internal stress σ_{calcd} is calculated from

$$\sigma_{calcd} = \int_{t_{vp}}^t E \times \gamma dt \quad (1)$$

The shear modulus G , rather than Young's modulus E , was measured in this work (Fig. 3). 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:

$$\sigma_{calcd} = 2.66 \int_{t_{vp}}^t G \times \gamma dt \quad (2)$$

The relation between the experimental and calculated values σ_{obsd} and σ_{calcd} of internal stress is shown in Figure 9. An essentially linear relationship existed between the observed and calculated internal stress regardless of the chemical structures of the networks. This result shows that the values of σ_{obsd} directly depend on the products of the elastic modulus and the shrinkage after vitrification of the cured resins. We conclude also from this result that the reduction of the internal stress with the introduction of larger substituent groups is due to the decrease of the shrinkage after vitrification.

CONCLUSIONS

Two-functional and four-functional epoxide resins were cured with various aromatic diamines. The ef-

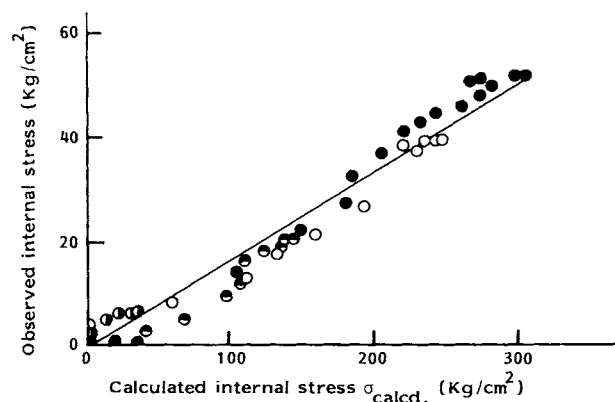


Figure 9 Relation between observed and calculated internal stresses in the curing process. Symbols as in Figure 3.

fect of the functionality of epoxide resins and the chemical structure of aromatic diamines on the internal stress of these cured systems was investigated in detail. The following conclusions were obtained:

1. The internal stress in the two-functional resin system is observed only in the cooling process. However, the stress for the four-functional resin systems is observed in both the curing and cooling processes. The reason for this result is that the latter systems have high glass transition temperature and, thus, vitrify in the course of the curing process.
2. The internal stress of four-functional resin systems was reduced with the introduction of larger substituent group into curing agents, even though the T_g 's of these systems are of similar value (above 300°C). The reduction of internal stress is explained as the result of the decrease of the shrinkage after the vitrification point in the curing process.

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