Contractive stress of epoxy resin during isothermal curing

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The contractive stresses of an amine curing epoxy resin during isothermal curing are studied by photoelastic and bimetallic methods. The increase in elastic modulus during the curing process of the resin is measured by torsional braid analysis (T.B.A.). The contractive stress in composite systems is observed only after gelation of the resin. The volume contraction after gelation is effective in generating contractive stress; the contraction in the fluid state is not effective. The effective contraction is estimated to be one third of the total contraction in this experiment.

INTRODUCTION

The volume of thermosetting resins such as epoxy resins decreases through both the process of curing and of cooling from the curing temperature. This volume contraction of the resin restrained in the composite system results in the occurrence of stresses. Such stresses often lead the materials to self-destruction or deterioration. The problem of residual stress is important for polymer processing. This problem, however, has been dealt with in only a few papers.

Among these few is the work by Dannenberg[1] who has studied the condition of the occurrence of the thermal stress and the second order transition temperature of the cured epoxy resins. In his paper, it is suggested that the stress caused by the contraction associated with the curing process was not observed. However, the experimental verification of the above suggestion is not found. The problem of occurrence of stresses in the isothermal curing process in which thermal stresses cannot occur remains unsolved.

In this paper, the condition of occurrence of stresses associated with the contraction of amine curing epoxy resin in isothermal curing processes is studied and discussed. On the surface of metals or glasses bonded by the perfectly adhering epoxy resin, the lateral contraction of the resin is restrained and leads to the occurrence of the contractive stress. For observation of the occurrence of the stress, both photoelastic and bimetallic methods are adopted in this experiment. In the photoelastic method, the resin is put in a transparent glass cell, and the isochromatic fringes are observed. In the bimetallic method, the deflection of a thin metal strip coated with the resin is measured. To discuss the mechanism of the occurrence of the contractive stresses, the following measurements are made isothermally: the volume contraction with a dilatometer, the increase in the elastic modulus by torsional braid analysis[2] (T.B.A.) and the gel fraction by methylethyl ketone (MEK) extraction.

EXPERIMENTAL

To observe the process of isothermal curing, most measurements are carried out at the temperature of 25 ± 0.5°C.

Materials

The following recipe of resin is used for optical measurement: Shell Epicote–828 as a resin (100 parts), 1,3 bisamino-methyl/cyclohexane (1,3 BAC) as a hardener (17 parts), allyl-glycidyl/ether (AGE) as a diluent (12 parts). To retard the chemical reaction and to make evacuation easier, this amine curing system is diluted with the AGE. This resin shows a perfect wettability and an excellent adhesion to the metal and the glass surfaces.

Measurement of volume contraction

The sample (1 cc) enclosed with natural rubber membrane (0.1 mm in thickness) is put in the mercury/dilatometer regulated to the temperature of 25 ± 0.05°C for the measurement of decrease in volume of the reacting materials. This measurement is sensitive to change of above 0.012%. It is continued until further change in volume cannot be observed. Then the sample is removed from the cell for the measurement of the weight and density.

Observation of contractive stress by the photoelastic method[3]

If materials are transparent and optically isotropic, all of plane polarized incident light on the materials is propagated without effect on the polarization or the phase. The stresses occurring in the materials decompose the transmitted light into two components with different velocity polarized in the direction of the principal axes of the stresses. This phase difference is detected and shown as photoelastic fringes with the photoelastic apparatus. The fringe order, N, and the principal stress difference, $(\sigma_1 - \sigma_2)$, are related as:

$$\sigma_1 - \sigma_2 = N/\alpha t \qquad (1)$$

where σ_1 and σ_2 are the principal stresses, α is the photoelastic sensitivity and t is the thickness of the sample.

As the contraction of the resin put in a glass cell is restrained at glass–resin boundaries, the contraction cannot be uniform and leads to a stress distribution. In this case, the sample will not be in a state of plane stress, but the isochromatic fringe order can be thought to correspond to the stress difference integrated along the light path. The occurrence

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of stresses is detected from the appearance of the isochromatic fringes.

To keep the deformation of a sample cell as small as possible, it is made of thick optical glass (20 mm). The inside size of cell is 30 x 35 x 20 mm (breadth, depth, thickness).

Observation of contractive stress by the bimetallic method

In the bimetallic method, the thin steel strip (180 x 13 x 0.05 mm) coated with the resin on the upper surface is placed on the two knife edges (span 90 mm). The value of the deflection, δ, of the strip caused by contraction of the coated resin is measured.

To obtain the contractive stress, σ_b, in the resin at the initial stage of curing, the following considerations are made. Since the contractive force, f, is very small at the initial stage, the shift of neutral axis of the bending strip can be considered negligible, and the contractive force acts tangentially along the upper surface of the metal strip. The bending moment, M, caused by this force is given by:

$$M = \frac{1}{2}hf \qquad (2)$$

where h is the thickness of the metal strip. This moment is equilibrated with the moment of the bending strip as:

$$\frac{1}{R} = \frac{M}{E_m I_b} \qquad (3)$$

where R is the radius of the curvature of the bending strip, E_m is Young's modulus of the metal strip and I_b is the moment of inertia of area of the metal strip. This is given by:

$$I_b = \frac{bh^3}{12} \qquad (4)$$

where b is the width of the metal strip.

Since the deflection of the bending strip is much smaller than the radius of the curvature of the bending strip, then the following geometrical relation holds:

$$\frac{1}{R} = \frac{8\delta}{L^2} \qquad (5)$$

where L is the span of the two knife edges.

From equations (2), (3), (4) and (5), the contractive force of the resin is obtained as:

$$f = \frac{4bE_m h^2\delta}{3L^2} \qquad (6)$$

On the assumption that the stress distribution in the resin layer is uniform, the stress is given by:

$$\sigma_b \equiv \frac{f}{bd} = \frac{4E_m h^2\delta}{3dL^2} \qquad (7)$$

where d is the thickness of the resin.

For further discussion, the following treatment will be useful. The apparent linear contraction, ϵ_a, which is brought about in the resin layer with bending of the strip, may be derived from consideration of the geometrical relation as:

$$\epsilon_a = \left(\frac{h}{2} + d\right)\frac{8\delta}{L^2} \qquad (8)$$

The effective strain of the resin, ϵ_e, generating the stress in the bimetal is thought to be the difference between the free linear contraction, ϵ_f, obtained by the dilatometry and the ϵ_a:

$$\epsilon_e = \epsilon_f - \epsilon_a \qquad (9)$$

Then, the Young's modulus of the resin, E_r, can also be calculated from ϵ_e and σ_b as:

$$E_r = \sigma_b / \epsilon_e \qquad (10)$$

Measurement of gel fraction of resin

The gel fraction of the resin during the curing process is measured. Uncrosslinked components are extracted by methyl-ethyl ketone (MEK) and insoluble components are weighed after drying. The gel fraction is obtained as the ratio of the insoluble components weight to the total resin weight.

Measurement of elastic modulus by the T.B.A. method

The elastic modulus of the resin is measured during the hardening process, from its liquid state to its solid state, by the torsional braid analysis method.

The frequency, ν, and the logarithmic decrement, λ, of a torsional pendulum are measured. The torsional pendulum is made of the inertia wheel and the glass braid impregnated with the resin. The impregnated glass braid is 100 mm long and 0.5 mm in radius. The braid is made of 16 yarns. A yarn (Asahi Fiber Glass Co. Ltd. ECE 225-1/0) consists of about 200 single filaments of 7 μ diameter.

The shear modulus, G, of the composite is calculated as:

$$G = (8\pi l I_t / r^4)\nu^2 \qquad (11)$$

where I_t, l, r and ν are the moment of inertia, the length of the specimen, the radius of the specimen and the observed frequency, respectively.

As it is difficult to eliminate the contribution of the glass filaments from the measured value of G, the relative shear modulus G_r of the composite system is recorded. The initial value of G_r is taken as unity.

The logarithmic decrement λ is determined from the ratio of two adjacent amplitudes:

$$\lambda = \ln(A_1/A_2) \qquad (12)$$

where A_1 is any amplitude, A_2 is the next amplitude.

RESULTS

Reaction times were measured from the beginning of the reaction started by mixing of the materials.

From the results of dilatometry, most of the reactions were completed in 14 h. The volume contraction was measured to be 2.47% after 6 h and to be 3.55% after 300 h (*Figure 1*).

The isochromatic pattern is shown in *Figure 2*. At the first stage of the observation, the whole field was dark. The fringes initially appeared in both upper corners where the free surface contacted with the wall of the cell (*Figure 2a*) and spreaded successively over the field. The spread fringes finally converged near both lower corners (*Figure 2b*). The isochromatic fringes could be observed after 6 h. The increase in N was observed for 30 h (*Figure 3*). Further generation of the fringes was not observed after 300 h. To estimate the value of the contractive stress from the observed isochromatic fringe, the value of the photoelastic sensitivity α is required. The value of α changes during the reaction, and it is difficult to follow the values of α. The value of α for the completely cured epoxy resin is measured as 0.85 (mm/kg) from a tensile test. Provided that the value of α is kept constant at the above value, the maximum stress at the upper corner is estimated as 47 (kg/cm^2) after 30 h.

The stress obtained by the bimetallic method σ_b was observed to occur after 6 h and to increase continuously

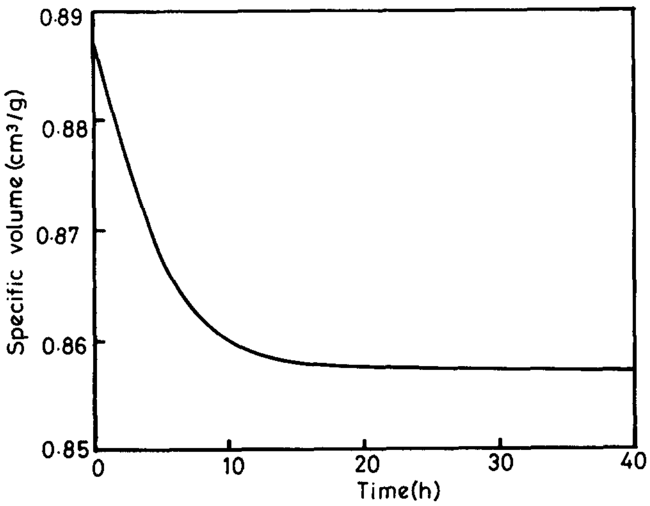

Figure 1 Reaction time vs. specific volume

(*Figure 4*). The value of σ_b was estimated from equation (7) and the following values; E_m: 2.1 x 10^6 kg/cm^2, h: 0.05 mm, d: 1.0 mm and L: 90 mm. The value of 1 mm in δ corresponds to the value of 0.86 kg/cm^2 in σ_b for example. The values of δ and σ_b were obtained as 1.3 mm and 1.1 kg/cm^2 after 30 h respectively. The values of ϵ_a, ϵ_f and ϵ_e were estimated as 0.13%, 0.36% and 0.23%, respectively. Then the value of the modulus E_r of the resin was estimated as 4.8 x 10^2 kg/cm^2.

The gel fractions could be detected after 5 h, and were measured to be 70% after 10 h and 80% after 12 h. Then the observed value of gel fraction asymptotically reached 90% (*Figure 5*).

The relative shear modulus G_r obtained by the T.B.A. method began to rise after 4 h, continued to increase, and showed slight and smooth increase after about 15 h, while the logarithmic decrement λ showed two peaks after 1 and 5 h (*Figure 6*). The absolute value of G of completely cured resin without braid was estimated to be 6.9 x 10^3 (kg/cm^2) from the equation (11) after 30 h. Provided that

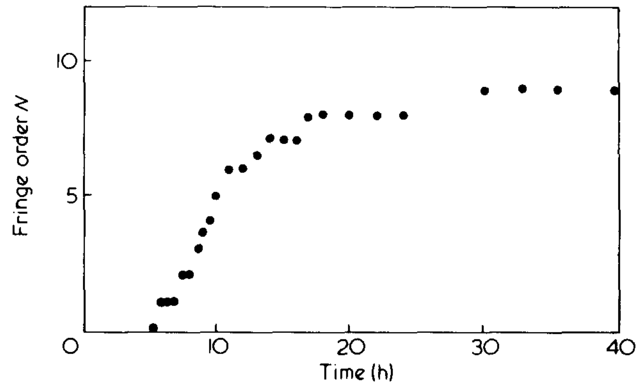

Figure 3 Reaction time vs, photoelastic fringe order N

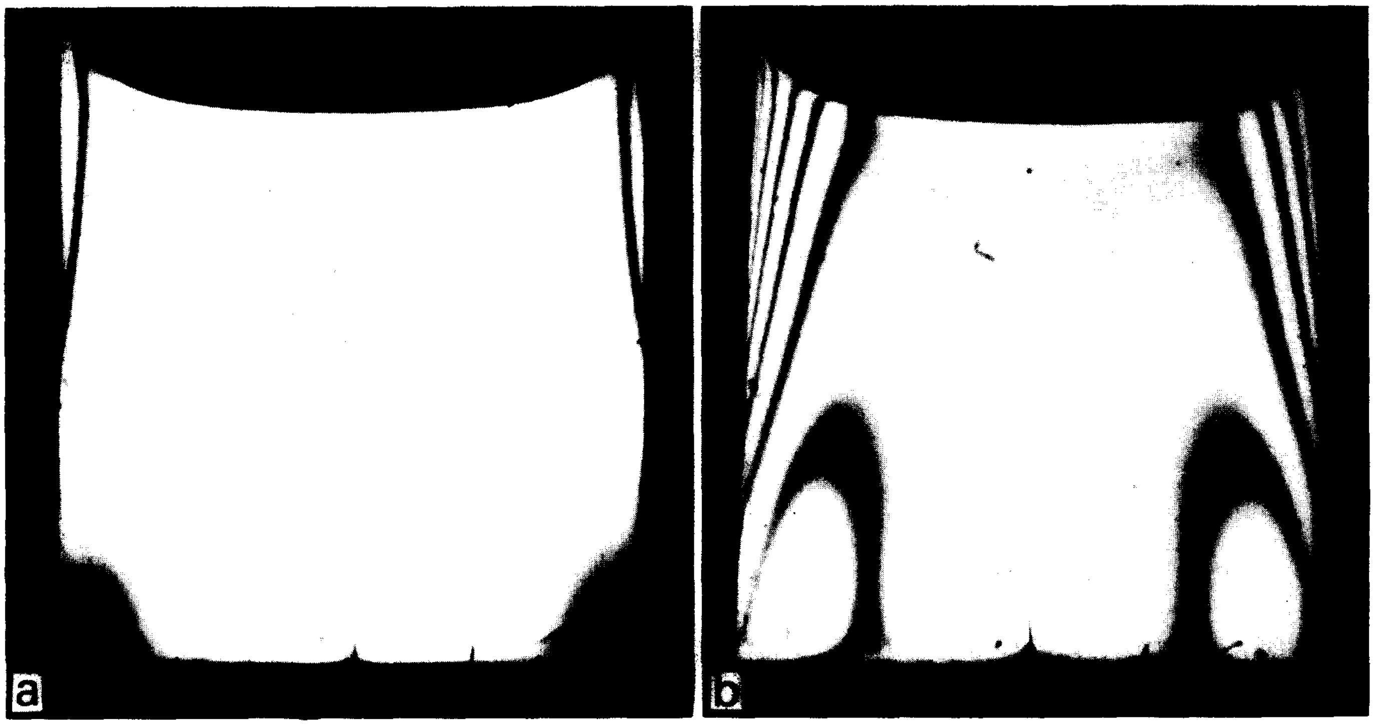

Figure 2 Isochromatic patterns for the resin in the cell; (a) after 7 h, both the upper dark lines are the first order fringes, the zero-th order fringes remain at the lower corners; (b) after 30 h, up to the eighth order fringes are observed, the 8-th order fringes appear at the both upper corners

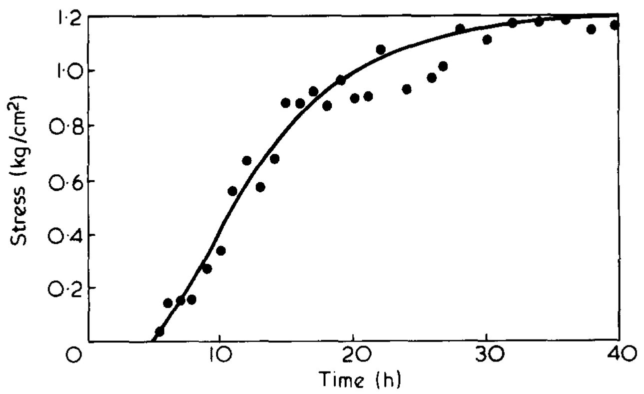

Figure 4 Reaction time vs. stress in coated resin

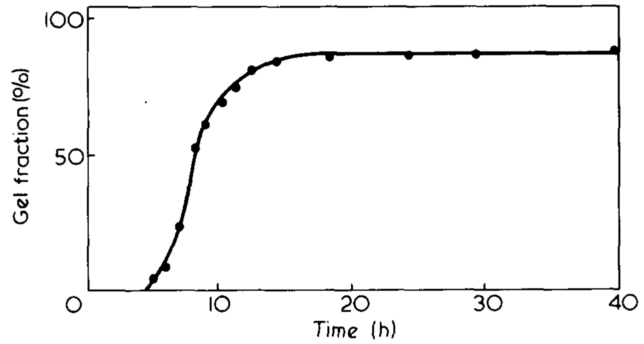

Figure 5 Reaction time vs. gel fraction

the Poisson's ratio is 0.5, the Young's modulus, E_T, becomes 3G. The value of E_T after 30 h was estimated to be 2.1 x 10^4 (kg/cm^2).

DISCUSSION

The volume contraction is observed immediately after the beginning of the curing reaction. On the contrary, the contractive stresses are observed to occur coinciding with the rise of G_r and the start of the gelation.

The occurrence of the contractive stresses requires both the existence of a volume contraction and of an elastic modulus. The gelation of the resin is necessary to generate the contractive stress; the contraction in the fluid state is not effective in generating stresses. Only the volume contraction after gelation is effective in generating stress. This volume is estimated to be 0.90% which corresponds to one third of the total volume contraction in this experiment.

In an isothermal curing process, the essential factor for the occurrence of the residual stresses is the volume contraction caused after the gelation that leads to the vanishing of fluidity and the remarkable increase in the elastic modulus of the resin.

To explain the relationship among the observed stresses, contraction and moduli, we now examine the value of them after 30 h when the curing reaction is regarded as being almost completed. This time is indicated by the fact that the appearance of further order fringes cannot be observed.

The values of the stress are obtained as 47 (kg/cm^2) by the photoelastic method, as 1.1 (kg/cm^2) by the bimetallic method and as 83 (kg/cm^2) by calculation from the free linear contraction (0.36%) and the Young's modulus of the resin (E_b: 2.3 x 10^4 kg/cm^2) measured by bending test. It must be asked why the value of the stress by the bimetallic method is extremely small compared with the others. It is noted

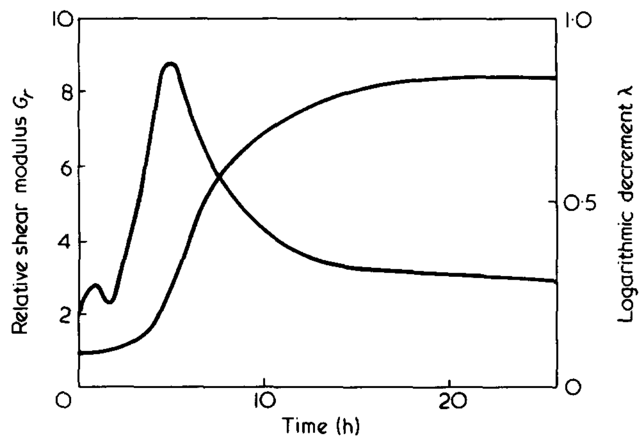

Figure 6 Reaction time vs. relative shear modulus G_r and logarithmic decrement λ

that the observed contractive stresses depend on the restraint condition. However, the extreme differences between them cannot be explained only from the consideration on the restraint condition in the bimetallic method (Cf. result).

In the bimetallic method, the stress governed by the relaxed modulus (equilibrium modulus) under the restraint condition is thought to be measured. The equilibrium modulus is estimated to be 4.8 x 10^2 (kg/cm^2) with this method. On the other hand, the modulus E_T by the T.B.A. method (regarded as the instantaneous modulus) is estimated as 2.1 x 10^4 (kg/cm^2), which was comparable with the value of E_b by bending test.

In the photoelastic method, the stress is measured under the tight restraint condition which brings about major relaxation of the resin. Nevertheless this value is comparable to the above calculated value of the stress. Therefore flow or orientation of molecules frozen according to the gelation is measured rather than the stress in the photoelastic method.

However, the photoelastic and bimetallic methods may be recommended as methods of observing the occurrence of the contractive stresses.

The occurrence of the stresses is essentially subject to the behaviour of the elastic modulus. Thus the observation of the elastic modulus during the reaction by T.B.A. method is thought to be a most useful technique.

CONCLUSION

In an isothermal curing process of an amine curing epoxy resin, the contractive stress occurs after the gelation of the resin.

The increase in elastic modulus associated with the gelation is the decisive factor in the occurrence of the contractive stress rather than just the volume contraction itself.

The volume contraction after gelation is effective in producing contractive stresses. In these experiments, the value of the total volume contraction and the effective volume contraction are estimated to be 3.55% and 1.08% respectively.

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