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GENERATION OF INTERNAL STRESS IN THE PROCESS OF SOLIDIFICATION OF SYNTHETIC RESIN, I

Internal Stress caused by Contraction

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When casting resin is cured, the volume contraction takes place from the bridge forming reaction and cooling. When the contraction is caused being free from restraint, the internal stress will not originate, but if geometrically restrained, it will originate.

In this report, the relation between the free contraction during the curing process and the internal stress caused by the geometrical restraint is studied on the casting type epoxy resin, and the behavior of the resin related to the cause for the origination of internal stress is considered.

Introduction

As for the polymers, such as unsaturated polyester or epoxy resin, used for casting, when they are cured by adding a curing agent, the volume contraction takes place. This contraction takes place in the process of the curing reaction due to poly-addition and in the process of cooling from the reaction temperature to room temperature. When these contractions are not restrained geometrically and are caused freely, the internal stress will not originate, but if geometrically restrained, it will originate. The free contraction of resin will depend upon the composition and curing conditions of the resin, *etc.*, but it is expected that the internal stress originating from contraction will further vary according to the form of restraint. Therefore, in order to elucidate the fundamentals for using casting resin, it is very important to study the relation between the geometrically free contraction during the curing process and the internal stress originating from geometrical restraint. This study has been carried out for this purpose.

The measurement of the internal stress originating during the curing process, has been reported by Bush[1], Sampson *et al.*[2] and by Gutowsky *et al.*[3] The former two reports were concerning the measurement by dipping a hollow stainless steel cylinder with strain gauges in resin and the latter concerning the measurement of variation of quadrupole moment of Cu due to pressure after dispersing fine powder of Cu_2O in resin. In all these reports, the contraction of resin was restrained locally by means of the sensing element and the internal stress caused by contraction was measured, but there are no reports on study of the relation between the free contraction during

1) A. J. Bush, *Modern Plastics*, **35**, No. 6, 143 (1958)
2) R. N. Sampson and J. P. Lernick, *ibid.*, **35**, No. 6, 150 (1958)
3) H. S. Gutowsky and A. B. Robert, *J. Polymer Sci.*, **19**, 143 (1960)

curing process and the internal stress originating from being geometrically restrained.

In this report, first of all, for the both cases when the resin is cured freely from the restraint and when it is restrained*, the internal stress and the volume contraction are measured. Next, the volume contraction corresponding to the measured internal stress is calculated by using the elastic formula. And then from those mutual relations, it is considered, in the contraction during curing processes, which process contributes to the origination of internal stress and what kinds of behavior of the resin attribute to this origination.

In the near future, the behavior of resin molecules during the curing process will be studied by means of infrared spectrum.

Experimentals

Material and curing condition In this experiment, the epoxy resin cured with an organic acid anhydride was employed as the sample. That is, the epoxy resin was Epikote** #834 (epoxy eq.=252), which was the condensation product of epichlorohydrin and 2, 2-*bis*-(4-hydroxyphenyl)-propane, and the acid anhydride was *cis*-cyclohexane-dicarboxylic acid anhydride (mp.=35~36°C).

The combination ratio of epoxy group to anhydride was 1 mole to 0.9 mole.

For the curing temperature, 130°C was taken as the suitable one for measuring specific volumes of unreacted resin and cured one. Also, for the curing time, 72 hours were taken as enough time to complete the change of specific volume by the curing reaction at 130°C.

Experiment I. Method of measuring internal stress and volume contraction occurring during curing process in free model

In the case when the resin was cured freely from the geometrical restraint, the internal stress and the volume contraction were measured.

Method of measuring internal stress *Sample* The sample employed was free model, which was prepared in the same way as used in the following item.

Apparatus and procedure The same photo-elastic apparatus set with a thermostat oven was used and measurements were carried out for the same temperature range as used in the item on the method of measuring internal stress.

Method of measuring free volume contraction The free volume contraction was calculated from the measured relations between the specific volume and the temperature on unreacted resin and cured resin respectively.

(1) *Method of measuring the relation between the specific volume and temperature*

Sample As for the reacted resin, for measuring the specific volume at unreacted stage, the fresh sample was employed for each temperature. The resin and the curing agent were heated

* The model prepared without geometrical restraint during curing process will be called "free model", and that prepared by restraint "restrained model" throughout the present report.

** Epikote is the registered trade name of Shell Chem. Co.

to the measuring temperature separately and mixed just before the measurement.

The cured resin for free model was poured in a cylindrical container of teflon, sealed with silicone rubber and cured, for fear it might be restrained due to adhesion and curing agent might escape. After curing, both ends were removed. The fact that there is no internal stress at these parts is evident from the result of the experiment above mentioned.

Apparatus and procedure Measurements were carried out by using a density balance based on the replacement method. That is, the unreacted resin was a liquid and so the transparent quartz cylinder having the known density-temperature relation was immersed in it.

On the other hand, as the cured resin was a solid, it was immersed in a silicone oil having the known density-temperature relation. Temperature of the bath was adjusted within ±0.1°C.

On the unreacted resin, attention was paid to the following technique that the measurement was completed within 5 minutes after mixing. On the cured resin, the temperature was raised and lowered at the rate of 0.3°C per minute and for both processes, the measurements were carried out at the about 5°C intervals from 20°C to 145°C. Before every measurement, the temperature was kept constant for 30 minutes.

(2) *Calculation of volume contraction*

The volume contraction, for convenience of considering the result, is divided into the following three kinds and defined as the following formulas.

Reacting contraction: ratio of volume contraction caused by chemical reaction at curing temperature,

$$\text{Reacting contraction } (\%)=\frac{V_{l130}-V_{s130}}{V_{l130}}\times 100. \qquad (1)$$

Curing contraction: ratio of volume contraction occurring during the whole curing process,

$$\text{Curing contraction } (\%)=\frac{V_{l130}-V_{s20}}{V_{l130}}\times 100. \qquad (2)$$

Thermal contraction: ratio of volume contraction occurring during cooling process of cured resin from reaction temperature to room temperature,

$$\text{Thermal contraction } (\%)=\text{Curing contraction } (\%)-\text{Reacting contraction } (\%), \qquad (3)$$

where V_{l130} is the specific volume of the unreacted resin at 130°C, and V_{s130} is that of the cured resin at 130°C and V_{s20} at 20°C.

Experiment 2. Methods of measuring internal stress and volume contraction occurring during curing process in restrained model

In the case when the resin was geometrically restrained during the curing process, the internal stress and the volume contraction were measured. Also, the elastic modulus and the stress optical coefficient of the resin employed were obtained, as these properties are necessary to study the stress distribution and to calculate the contraction corresponding to it.

For the geometrical restraining, a mild steel rod was inserted in the center of the resin.

Method of mesuring internal stress *Sample* Mold is a steel pipe of 41 mm inner dia., 50 mm external dia. and 100 mm length, whose inside was treated with the releasing agent, and a mild steel rod of 10 mm external dia., 120 mm length was put in its center, and after being poured into the mold, the resin was cured.

After curing, a slice perpendicular to the center axis was machined from the middle part of the resin, and it was heated for removing the machining strain after grinding and then the slice was used for photo-elastic investigation. The dimensions of the restrained model are shown in Fig. 1.

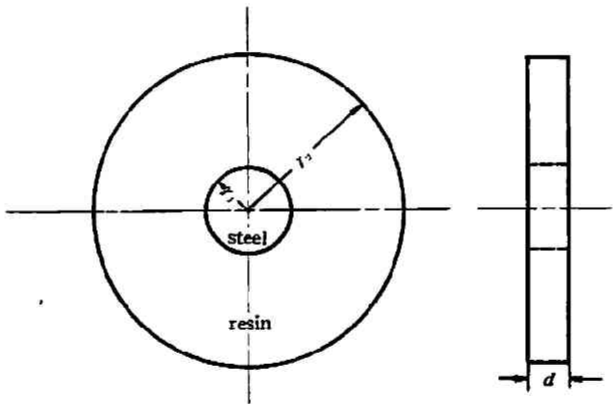

Fig. 1 Restained model

r_1 = 5.0 mm
r_2 = 20.2 mm
d = 5.08 mm

Apparatus and procedure The internal stress distribution was measured by photo-elastic stress analysis. For the measurement on iso-clinic line, a white light plane-polariscope was used and for that on iso-chromatic line, a monochromatic circular-polariscope was used at wave-length of 5461 Å. For obtaining the temperature effect, the thermostat oven adjusted within ±1°C between the polarizer and the analyzer was provided and the temperature was raised and lowered at a rate of 0.3°C per minute, the measurements were carried out at 10°C intervals from 15°C to 130°C and the temperature was kept constant at each measuring point for 30 minutes. Also, the fractions of fringe order were measured by Tardy's method[4].

Method of measuring volume contraction appearing during reaction process *Sample* Restrained model and mold for preparing the model were taken as sample.

Apparatus and procedure Using a comparator with 1/1,000 mm reading, the internal dia. of the mold and external dia. of the restrained model at 20°C were measured, while the external dia. of the restrained model and the mild steel rod at 130°C were measured with their photographs. From thess results, the inner dia. of the steel mold and the external dia. of the mild steel rod at 130°C were calculated by using the thermal expansion coefficient and further the external dia. of the restrained model at 130°C was calculated.

The volume contraction was calculated from Formula (4).

4) Ohryoku Sokutei Gijutsu Kenkyukai, *Ohryoku-Shokutei-Ho*, p. 535(1955), Asakura Shoten

$$\text{Volume contraction } (\%) = 3\times\frac{D_2-D'_2}{D_2-D_1}\times 100, \tag{4}$$

where D_2 is the inner dia. of the mold at 130°C, D'_2 is the external dia. of the model at 130°C and D_1 is the external dia. of the mild steel rod at 130°C.

Method of measuring temperature effects on elastic modulus and stress optical coefficient of cured resin *Sample* The specimens were prepared by machining the cured resin plate and then heated after polishing the surfaces by grinding.

Apparatus and procedure The measurement of the elastic modulus in the range from 15°C to 130°C was carried out by the bending method in the thermostat oven equipped with a dial gauge and a loading apparatus. The measurement of the stress optical coefficient in the range from 23°C to 160°C was carried out by the four points bending method[5], by means of the circular polariscope set in the thermostat oven equipped with the loading apparatus.

The stress optical coefficient was represented as fringe stress. In both cases the oven was adjusted within ±1°C at each measuring point.

Result

Result 1. Result of measurement on internal stress and volume contraction occurring during curing process in free model

Result of measurement on internal stress The photo-elastic fringe did not appear and it was considered that there was no internal stress.

Result of measurement on free volume contraction

(1) *Relations between specific volume and temperature on unreacted resin and cured resin* The results on unreacted resin and cured resin are shown in Fig. 2. From these results, the specific volume V_{l130} of the unreacted resin at 130°C was 0.9018 cc/g, the specific volume V_{s130} of the cured resin at 130°C was 0.8495 cc/g and the specific volume V_{s20} of the cured resin at 20°C was 0.8294 cc/g. Also, the second order transition point of the cured resin was 116°C, the upper limit of the transition range was at about 126°C and the lower limit at about 77°C. On the unreacted resin, judging from the fact that the measured value near 130°C was on the straight line extrapolated from the measured points at lower temperatures where the rate of reaction was extremely retarded, the specific volume of the unreacted resin at 130°C was considered to be measured in the unreacted stage.

(2) *Free volume contraction* The result obtained is shown in Table 1.

Table 1 Volume contraction in free model

Reacting contraction	(%)	5.80
Thermal contraction	(%)	2.25
Curing contraction	(%)	8.05

5) Reference 4) p. 512

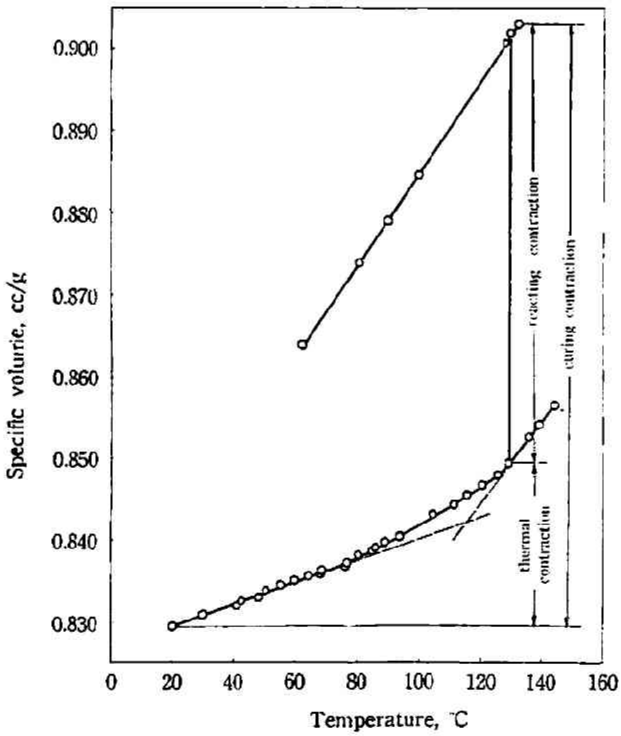

Fig. 2 Dilatometric properties for uncured and cured resins

Result 2. Result of measurement on internal stress occurred during curing process and volume contraction appeared during reaction process in restrained model

Result of measurement on internal stress One example of photographs on iso-clinic

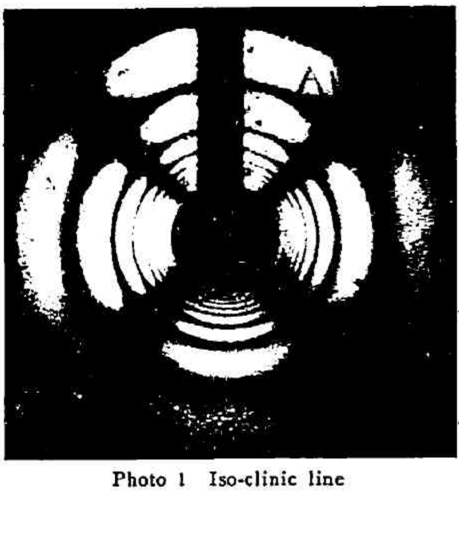

Photo 1 Iso-clinic line

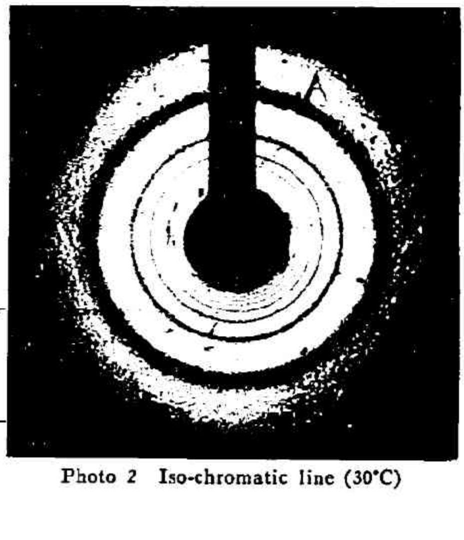

Photo 2 Iso-chromatic line (30°C)

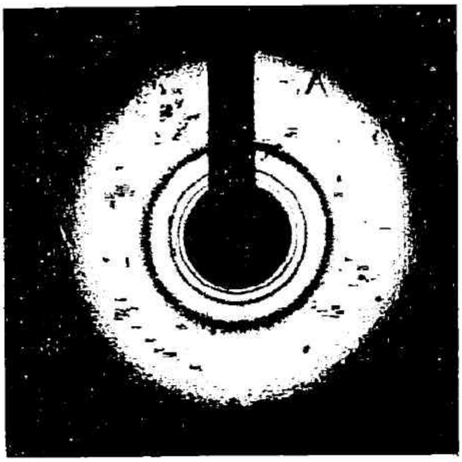

Photo 3 Iso-chromatic line (100°C)

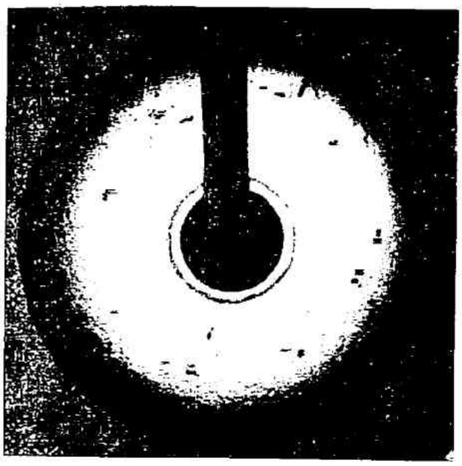

Photo 4 Iso-chromatic line (130°C)

line is shown in Photo 1, and those on monochromatic line at 30, 100 and 130°C are shown in Photos 2, 3 and 4. The iso-clinic line does not change at each temperature, but the monochromatic line varies.

That is, with lowering temperature, the number of fringes around the mild steel rod increase and the fringe order becomes higher. As for the free boundary around periphery, the color of

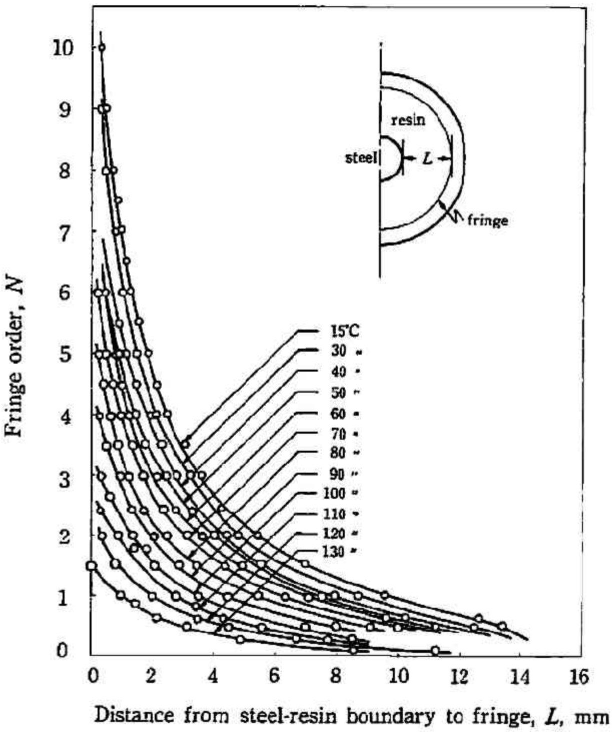

Fig. 3 Fringe-distribution in restrained model

fringe, as the result of inspection with white light, is black and so the fringe order is approximately zero. The fringe order distribution at respective temperatures is shown in Fig. 3.

Result of measurement on volume contraction appeared during curing process The results obtained are as follows,

$$D_1=0.999\,\text{mm},\quad D_2=41.051\,\text{mm}\quad \text{and}\quad D'_2=40.499\,\text{mm}.$$

The result obtained from Formula (4) is shown in Table 2.

Table 2 Volume contraction in restrained model

Volume contraction appearing during reacting process (%)	5.33

Results of measurement on temperature effects on elastic modulus and stress optical coefficient of cured resin The temperature effects on the elastic coefficient and fringe order of the cured resin are shown in Fig. 4.

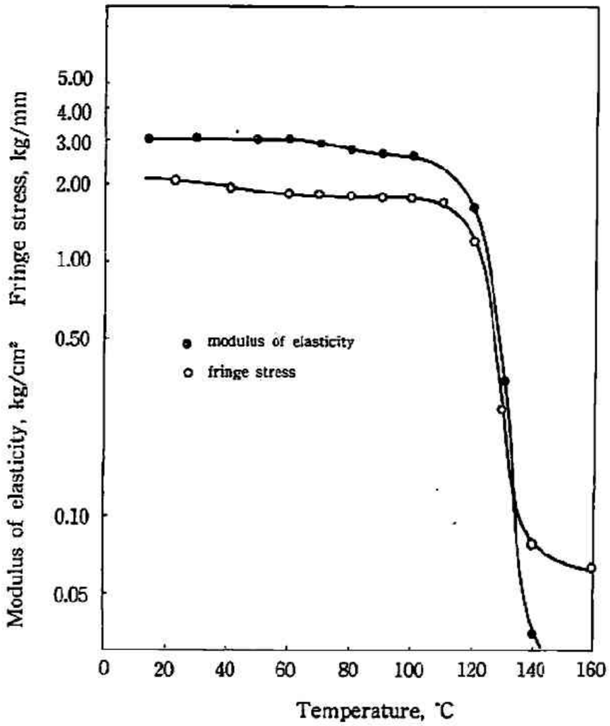

Fig. 4 Fringe stress and modulus of elasticity for the employed epoxy resin

Considerations

First, it was studied by what formula the distribution curve of internal stress shown in Fig. 3 should be represented. And from the result, the volume contraction corresponding to the internal stress occurring during the curing process was obtained by calculation.

Next, from the relation among the various kinds of volume contraction obtained from the experimental results and the calculated results, the considerations were made on the relation between the volume contraction appearing the curing process and the internal stress caused by restraining it.

On internal stress distribution occurring in restrained model and volume contraction corresponding to it

On internal stress distribution occurring in restrained model The stress distribution shown in Fig. 3 can be considered analogous to the case where a thick-walled cylinder with inner radius r_1 and outer radius r_2 subjected to the uniform pressure P on the inner face, and so it was studied whether the elastic formula was applied to this case or not. That is, at a radial co-ordinate, the fringe order N corresponding to the difference in the principal stresses $(\sigma_t-\sigma_r)$ at any radial location r is given by Formula (5).

$$N=(\sigma_t-\sigma_r)\frac{d}{S}=2P\frac{r_1^2\, r_2^2}{(r_2^2-r_1^2)r^2}\cdot\frac{d}{S}, \tag{5}$$

where S is the fringe stress, d the thickness of the sample. In Fig. 4, using the fringe order N corresponding to $L=5$ mm (10 mm as r), which is considered to give reliable data with respect to location, the inner pressure P was obtained from Formula (5).

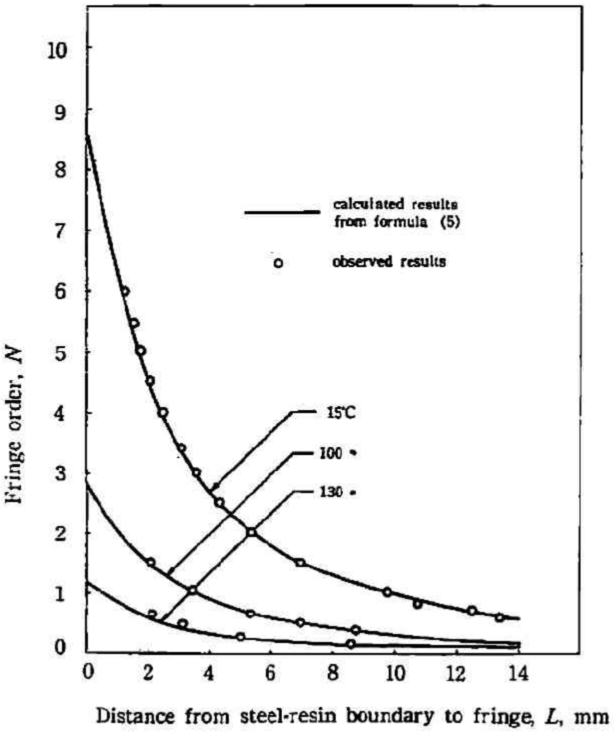

Fig. 5 Comparison between calculated and observed results of fringe distribution in restrained model

Using this P, the fringe order distribution at r was calculated from Formula (5), and compared with the observed results shown in Fig. 3, and then good agreement was obtained in both results.

As one example, the cases at 15, 100 and 130°C are shown in Fig. 5. In this fringe, the calculated result from Formula (5) is shown by solid lines and the observed fringe order by plots. From the results of these studies, it may be considered that Formula (5) represents successfully the experimental results shown in Fig. 3.

According to those results, the variation of the inner pressure P with temperature was obtained by using Formula (5) and the data of Fig. 3, and this is shown in Fig. 6.

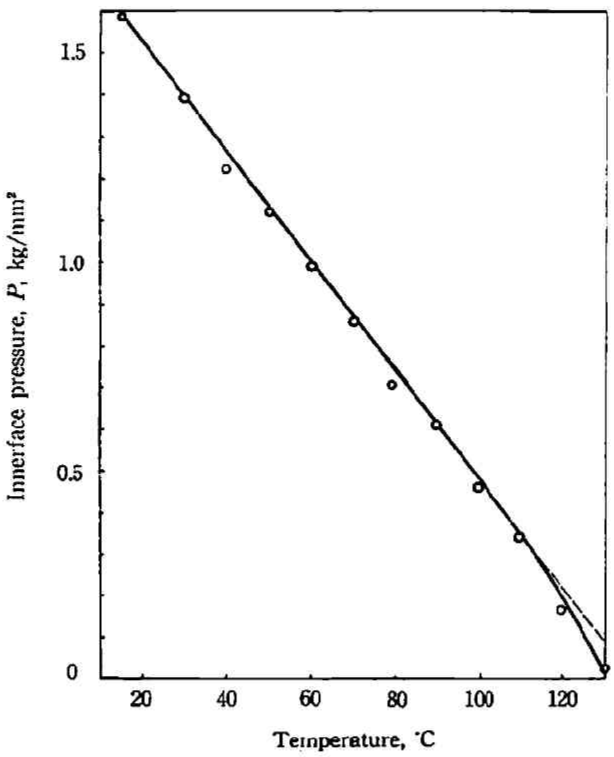

Fig. 6 Innerface pressure of restrained model

Volume contraction corresponding to internal stress distribution In the case when a mild steel rod having the same diameter as the inner diameter of a thick-walled cylinder is inserted in the center of the latter at temperature t_0, in stress-free condition, and when both are cooled down to temperature t, the interface pressure P between the resin cylinder and the mild steel rod is given by Formula (6)[6].

6) R. V. Southwell, *An Introduction to the Theory of Elasticity for Engineers and Physicists*, 2nd ed. p. 406–407 (1941), Oxford Univ. Press, London
G. Gerard and A. C. Gilbert, *Appl. Mech.*, 24, 355 (Sept., 1957)

$$\left.\begin{aligned} P &= \{(\varepsilon_t)_R-(\varepsilon_t)_M\}\Psi(t), \\ \Psi(t) &= \frac{E_R\, E_M(r_2^2-r_1^2)}{(1-\nu_M)E_R(r_2^2-r_1^2)+E_M\{(1+\nu_R)r_2^2+(1-\nu_R)r_1^2\}}, \end{aligned}\right\} \qquad (6)$$

where $(\varepsilon_t)_R-(\varepsilon_t)_M$ shows the difference of contraction for unit length of resin and mild steel rod when temperature varies from t_o to t, E_R and ν_R show elastic modulus and Poisson's ratio of resin and E_M and ν_M those of mild steel.

From this formula, the linear contraction $(\varepsilon_t)_R$ of resin is represented by Formula (7).

$$(\varepsilon_t)_R=\frac{P}{\Psi(t)}+(\varepsilon_t)_M. \qquad (7)$$

From this formula, the linear contraction $(\varepsilon_t)_R$ corresponding to the internal stress occurring at the state of 130°C and 20°C, *i. e.* at the states where reacting contraction and curing contraction had been finished respectively, was obtained and then the volume contraction was obtained. Also, from the difference between both, the volume contraction corresponding to the internal stress occurring during the thermal contraction process was obtained from Fig. 6, E_R was obtained from Fig. 4, ν_R was taken as 0.36 at 20°C and 0.40 at 130°C as the appropriate values for network type resin, and for E_M, ν_M, and linear expansion coefficient α of the mild steel, $E_M=2.12\times10^4\,kg/mm^2$, $\nu_M=0.26$ and $\alpha=11.2\times10^{-6}\,deg^{-1}$ [7]. Table 3 shows the calculated results of the inner face pressure P occurring during every process and the volume contraction corresponding to the internal stress.

Table 3 Innerface pressure P and volume contraction corresponding to internal stress

	Innerface pressure (kg/mm^2)	Corresponding volume contraction (%)
State when reaction process has been completed (130°C)	0.029	0.39
during cooling process (130°C~20°C)	1.49	2.26
State when whole curing process has been completed (130°C~20°C)	1.52	2.65

On relation of volume contraction occurring during curing process and internal stress caused by its restraining

On reacting process According to the various results obtained in the free model as described above, the internal stress was not observed during the reacting process and reacting contraction was 5.80% as shown in Table 1, while, in the restrained model, the observed contraction was 5.33% as shown in Table 2, and also, the innerface pressure was $0.029\,kg/mm^2$, and the corresponding contraction was 0.39% as shown in Table 3 and the difference from that of the free contraction was 5.41%.

7) Nihon Gakujutsu Shinko-kai, *Kinzoku-Zairyo IV*, p. 20 (1938), Iwanami Shoten

This value coincides comparatively well with the value 5.33% in Table 2. Accordingly, from the results, it may be said that, during the reaction process, by restraining of the free contraction, larger part of free contraction will appear outward as contraction, but a smaller part remains as the internal stress.

During the reaction process, resin molecule will gradually become larger while being accompanied by volume contraction, and the relative motion between the atoms in a molecule will be restrained by the first order bonding. When the contraction is not restrained, the random and stable configuration of the molecule may be taken, and then the internal stress does not originate. On the other hand, when the contraction is restrained, at the initial and intermediate stages of the reaction process, the random and stable configuration of molecule may be taken easily owing to easiness of inter- and intramolecular flow.

However, at the last state, when the network has spread, the random and stable configuration of molecule may be restricted, and then the stress attributed to entropic elasticity will originate.

On cooling process From the various results obtained in the free model as described above, the internal stress during this process was not observed and the thermal contraction as shown in Table 1 was 2.25%, while, in the restrained model, the innerface pressure was 1.49 kg/mm^2, and the corresponding contraction was 2.26% as shown in Table 3.

Both the values of contraction coincide well. Accordingly, from the result, it may be said that, by restraining of free contraction, the main part of it remains as internal stress during the cooling process.

During the cooling process, the micro-Brownian motion of molecular chain becomes gradually slow with the decrease of temperature, and when the second order transition range is passed, the molecular configuration taken at entropic elasticity region is frozen by intermolecular force.

When the contraction undergoes freely from restraint, the random and stable molecular configuration taken during the reaction process is maintained to be frozen, and then the internal stress does not originate.

When the contraction is restrained, the districted molecular configuration is maintained to be frozen, and additionally the molecular chain is more strained by thermal contraction.

And then, in a higher region than the second order transition range *i.e.* 126~130°C, the internal stress attributed to entropic elasticity originates. The stress originated in this region is generally considered to be relaxed, but in this case such a relaxation is not observed. This is understood from the facts that the employed resin is of network type, and its upper limit of the second order transition range is at about 126°C and accordingly the thermal strain caused by contraction in this region is small. When the second order transition point is passed, the already originated stress is frozen and the internal stress is originated by the thermal contraction.

In the lower region than the second order transition range, the internal stress is originated by the thermal contraction. This internal stress is considered to be attributed to the energetic elasticity, and caused chiefly by the change of rotation angle of molecular chain.

The results may be summarized as follows:

1) When the casting resin is cured, the volume contraction is caused by the bridge forming

reaction and cooling. When this volume contraction takes place, being free from geometrical restraint, the internal stress is not observed, but if this free volume contraction is geometrically restrained, the internal stress is observed by means of photo-elastic analysis.

2) As carried out in this study, when the innerface is geometrically restrained and the outerface is free from restraint, during the reaction process, the internal stress corresponding to extremely small part of free contraction occurs, and during the cooling process the internal stress corresponding to almost the whole part of free contraction occurs.

Acknowledgement

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