Effect of Temperature Gradients on Cure and Stress Gradients in Thick Thermoset Castings

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Synopsis

The temperature gradient developed during casting of an unsaturated polyester for which the kinetics of reaction and the heat capacities, thermal conductivities, and densities were known from earlier work was measured experimentally as a function of time in a thick casting and compared with predicted values calculated from a mathematical model. Agreement was excellent. The castings were sectioned and the sections were examined by birefringence. These examinations show good agreement between the temperature gradient developed during cure and the residual stress gradient. This work demonstrates that the extent of cure as a function of position can be predicted from heat transfer calculations if the reaction kinetics and thermal properties are known and that the residual stress gradient is dependent upon the temperature gradient developed.

INTRODUCTION

Thermosets are generally polymerized and processed in a single operation which involves the irreversible transformation of a low molecular weight resin into a network polymer. Examples include processes such as casting, potting, encapsulation, lamination, and thermoset injection molding. The crosslinking reaction is dependent upon the temperature, the type of resin, and the relative concentrations of monomer or prepolymer and initiator or curing agent.

Curing can be affected by changing the initiator or curing agent concentration. However, it is difficult to predict the effect of initiator concentration, since free-radical initiation is a complex process with competing reactions. Increasing the initiator concentration increases the rate of polymerization at a particular temperature, but since its concentration is established prior to the curing operation it does not provide a direct means for controlling the reaction.

The curing reaction of most thermosets is very exothermic. Since polymers exhibit low thermal conductivity, the temperature and rate of reaction can vary considerably within the curing mass, particularly for thick castings. For example, it has been reported that the crosslinking reaction of a typical unsaturated polyester generates as much as 150 calories per gram, which can result in peak exothermic temperatures of up to 260°C.[1] Therefore, the extent of reaction (or the "degree of cure") is a function of time and position, as determined by the balance of internal heat generation from the curing reaction, conduction, and heat exchange with the surroundings.

In the case of unsaturated polyesters, the curing is the result of free-radical-initiated reaction between a vinyl monomer (usually styrene) and fumeric or

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maleic acid double bonds in the polyester resin.[2,3]   Because of gelation, the re-
action becomes diffusion controlled,[4] and reaction (curing) never goes to com-
pletion; the extent of reaction depends upon the time–temperature history.   It
has been reported that 92 to 95% reaction can be considered to be the highest
cure to be expected, even under the best of conditions.[1]

Although no definitive studies have been made, it has long been evident that
large temperature differences with a casting during cure can lead to cracking or
crazing.   Mold temperature control and postcuring or annealing steps have been
used to attempt to develop uniform cure and properties within a casting.   Dy-
namic mechanical testing methods have been used to experimentally measure
mechanical properties during the later stages of cure.[5]   It has also been shown
that mechanical properties change with the time–temperature history of cure
during the early stages by using torsional techniques.[6]

It is therefore quite likely that the extent of reaction in a casting varies with
the differing local thermal histories within the polymer and that the local me-
chanical properties vary.   This variation could possibly be controlled by con-
trolling the curing temperature environment and the cure time.   Clearly, both
heat transfer and the reaction kinetics must be considered together to obtain
a complete process model to permit the curing process to be controlled.

There are a number of descriptive reports in the literature concerning the
theory of reaction molding processes, but there are only a few analytical studies
of the problems of nonuniform reaction due to both heat transfer and the reaction
exotherm during these processes.   In 1966, Stonecypher et al.[7] applied transient
heat transfer concepts to the curing of highly exothermic solid propellants and
developed a mathematical model for the curing process by which the curing
performance could be simulated.   In 1971, Hills[8] reported some transient heat
transfer calculations used to predict cure development in thick sections of rubber
molding.   Engelmaier and Roller[9] also used transient heat transfer along with
a time and temperature-dependent viscosity to model thickness changes in epoxy
electrical laminates.   Very recently, Broyer and Macosko[10] proposed a theoretical
model for curing in polymer reaction molding operations.   They also studied
the variations of certain physical properties with position and time in the mold
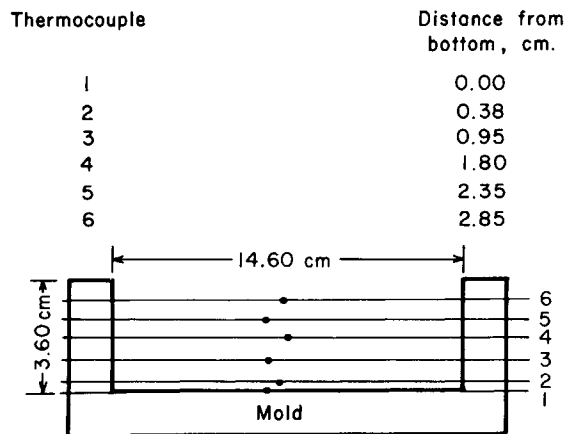for a typical urethane system.   Recently, Lee and Macosko[11] constructed a

Fig. 1. Experimental mold arrangement showing thermocouple placement.
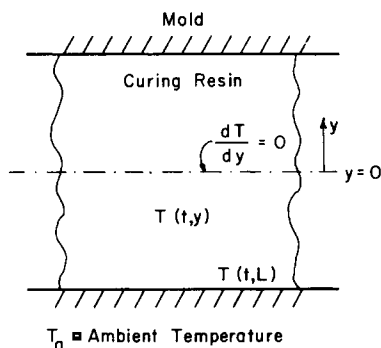
Fig. 2. Coordinate system for modeling of cure.

laboratory-size RIM machine with an instrumented slab mold and studied the temperature profiles developed for a urethane system.

The purpose of this work was to show that the temperature gradients developed in the polymer mass could be predicted if the kinetics of reaction and the physical properties of the polymer were known and to show the effects of these temperature gradients on the gradients of strain and extent of cure in thick castings. A general-purpose unsaturated polyester was chosen for which the kinetics of reaction[12] and the heat capacity, thermal conductivity, and density[13] had previously been experimentally determined.

EXPERIMENTAL

Materials

Polyester Resin. A general-purpose unsaturated resin supplied by Ashland Chemical Co., Columbus, Ohio, was used in this investigation. Styrene, used as the crosslinking agent, was determined to be 28% by weight with an accuracy of ±2%, by heating a 5-g sample of fresh resin in an oven at 110°C until constant weight was attained.

Catalyst (Initiator). A 60% solution of methyl ethyl ketone peroxide in dimethyl phthalate (Lupersol DDM) was used to initiate the crosslinking reaction. It was supplied by Pennwalt Co., Lucidol Division.

Promoter. Room temperature reactions were performed by activating the peroxide catalyst with cobalt naphthenate (6%) supplied by Troy Chemical Co.

Casting and Temperature Measurements

Experimental Setup. The experimental setup for the temperature measurements consisted of a silicone rubber mold, thermocouples, and a PDP-11 digital computer for data acquisition. A silicone rubber mold was prepared from a stainless steel mold pattern. Its inner dimensions were $6 \times 6 \times 1\frac{1}{2}$ in. A top cover with the same thickness as the mold base was also prepared.

The temperature-sensing assemblies were prepared from 30 AWG iron/constantan thermocouple wires. Each sensing assembly had its own measuring and reference junctions, and more than 30 thermocouples were prepared in this way. The experimental arrangement is shown in Figure 1.

The proper spacing between the measuring junctions was determined from a study of several approximate solutions for the temperature profiles that might be created inside the polymer mass as a result of the presumed unidirectional heat flow during casting. The measuring junction of each thermocouple was then placed at its previously determined location along the depth of the mold. The wires were fastened firmly at the mold edges to hold the position of the junction against the contraction and expansion forces during casting. The positions of the measuring junctions were also checked after casting operations to make sure that they had not been disturbed during the measurements.

Data Acquisition. The thermocouple signals were amplified and sent to a PDP11/40 minicomputer equipped with a 10-bit A/D converter. The time interval between readings was selected as either 3 or 5 sec. In each time interval, the computer took eleven points from each channel, averaged them, and stored them in a disk file for later analysis. After the experimental run was completed, calibration factors were applied to the raw data to convert them to actual temperature values.

Experimental Procedure. Calibration curves for each thermocouple were obtained over the temperature range of interest by using a constant-temperature bath. An ice bath was maintained for the reference junctions. Before each experiment, at least 10 thermocouples were calibrated, and the ones which had the most reproducible calibration curves were employed. The measuring junction of each thermocouple was placed in the mold as described above, and the vertical distance from the bottom surface of the mold was carefully measured.

The system employed in this investigation contained 100, 0.70, and 0.25 parts by weight of polyester, catalyst solution, and promoter, respectively. The required amounts of the resin mixture, catalyst, and promoter were weighed separately and were then mixed thoroughly in a large glass beaker (2 liter) for about 1 min. The catalyzed mixture was poured into the mold and the surface was covered with the mold top. At the same time, the computer program was ini-
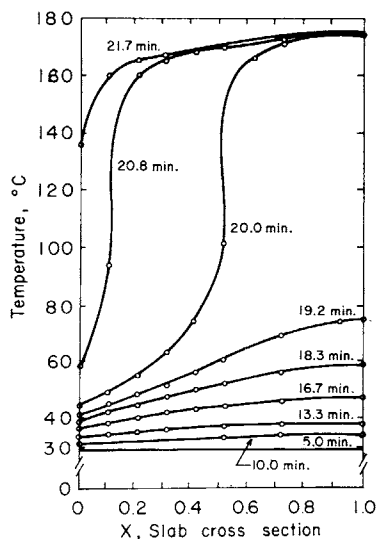

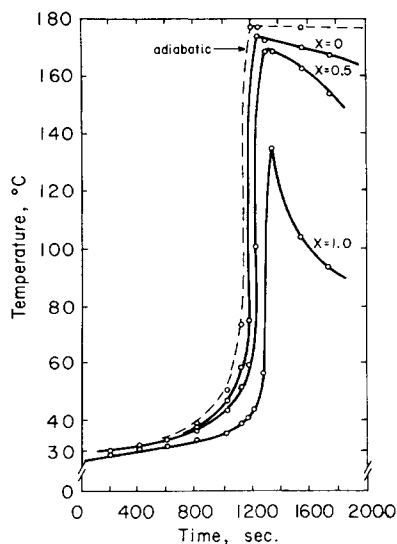Fig. 3. Calculated temperature changes at various locations in the curing polymer.

Fig. 4. Calculated temperature profiles (X = 1.0 represents center of slab).

tiated for temperature logging. It was also necessary to note the time for mixing and filling stages to keep their records for later data analysis. The total time for mixing and filling was about 110 sec, which was small compared to the reaction time.

The polymerization process was observed by watching the thermocouple outputs on the CRT screen. The exothermic crosslinking reaction proceeded for about 20 min. The polymer at the center reached its maximum temperature, 177°C, in about 22 min. The surface temperature at this time was recorded as 90°C, and it reached its peak temperature, 136°C, with a 100- to 120-sec time delay. The polymer started to cool after the heat generation, since the reaction had ceased. Later, the castings were sectioned and birefringence studies were made.

Mathematical Modeling

The following are the basic assumptions made in developing a model for the curing process: (1) no flow, (2) no mixing, (3) no molecular diffusion, and (4) one-dimensional heat conduction.

The most general treatment of the problem of transient heat conduction, including nonuniform and variable heat generation in the conducting body, can be represented[14] as

$$\rho C_p \frac{\partial T}{\partial t} = \nabla \cdot k_T \nabla T + G(x,y,z,t) \tag{1}$$

where G is a function representing that part of the temperature change due to the generation of heat within the curing mass.

Since the walls of the mold were quite far from the thermocouple junctions, only temperature gradients perpendicular to the mold walls (i.e., the y-direction) were considered to be significant. Thus, the energy equation reduces to

$$\rho C_p \frac{\partial T}{\partial t} = \frac{\partial}{\partial y} \left(k_T \frac{\partial T}{\partial y} \right) + G(y,t) \tag{2}$$
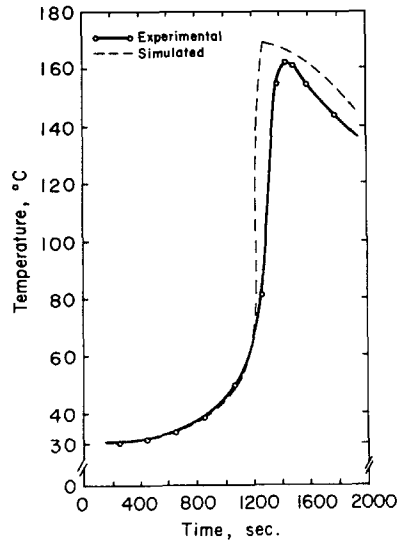
Fig. 5. Comparison of experimental (O—O) and simulated (---) temperature changes at the center of the curing polymer (X = 1.0).

where ρ is the resin density, C_p is the specific heat, and k_T is the thermal conductivity.

The volumetric internal heat generation rate $G(y,t)$ was assumed to be proportional to the curing reaction rate. That is,

$$G(y,t) = \rho \Delta H_R \frac{\partial P(y,t)}{\partial t} \tag{3}$$

where ΔH_R is the total heat release per unit mass of resin and P is the fraction polymerized.

The rate of polymerization is

$$\frac{\partial P}{\partial t} = k\, f(P) \tag{4}$$

where k is the rate constant and $f(P)$ is a function representing the amount of resin reacted and order of reaction.

It was assumed that the reaction rate followed the Arrhenius relationship. Thus, the general mathematical model of the curing process is defined as

$$\rho C_p \frac{\partial T}{\partial t} = \frac{\partial}{\partial y}\left(k_T \frac{\partial T}{\partial y}\right) + \rho \Delta H_R A\, e^{-E_a/RT} f(P) \tag{5}$$

$$\frac{\partial P}{\partial t} = A\, e^{-E_a/RT} f(P) \tag{6}$$

Formulation

The model was formulated by introducing the following dimensionless quantities:

$$\theta = \frac{T}{T_0}$$

$$X = \frac{y}{h}$$

$$\tau = \frac{\alpha}{h^2}t \quad \text{where } \alpha = \frac{k_T}{\rho C_p^0}$$

$$B = \frac{E_a}{RT_0}$$

$$C = 1 - P$$

where C is the fraction of uncured resin. Variation of specific heat with temperature is defined as

$$\frac{C_p}{C_p^0} = 1 + a(T - T_0)$$

where C_p^0 is the specific heat at T_0 and is a constant.

The thermal properties, the heat of reaction, and a kinetic expression of the curing reaction for the same polyester system have been developed and reported very recently.[12,13] From these studies the kinetic model was developed as

$$\frac{dP}{dt} = A \exp(-E_a/RT)P^n(1 - P)^m \tag{8}$$

where n = 0.5, $m = 1.5$, $E_a = 17.04$ kcal/g mole, and $A = 2.60 \times 10^9$ min^{-1}.

After substituting the above kinetic model and using the dimensionless variables, the governing equations, eqs. (5) and (6), became

$$\frac{\partial\theta}{\partial\tau} = \frac{1}{[1 + aT_0(\theta - 1)]}\frac{\partial^2\theta}{\partial X^2} + \frac{\Delta H_R K' e^{B(1-1/\theta)}(1 - C)^{0.50}C^{1.50}}{T_0 C_p^\circ[1 + aT_0(\theta - 1)]} \tag{9}$$

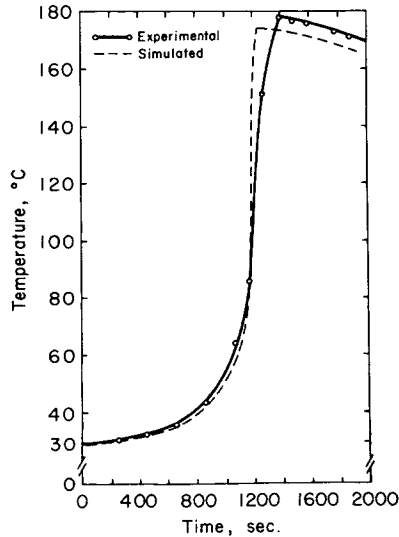$$\frac{\partial C}{\partial\tau} = K'e^{B(1-1/\theta)}(1 - C)^{0.50}C^{1.50} \tag{10}$$

Fig. 6. Comparison of experimental (o——o) and simulated (- - -) temperature changes at X = 0.5.
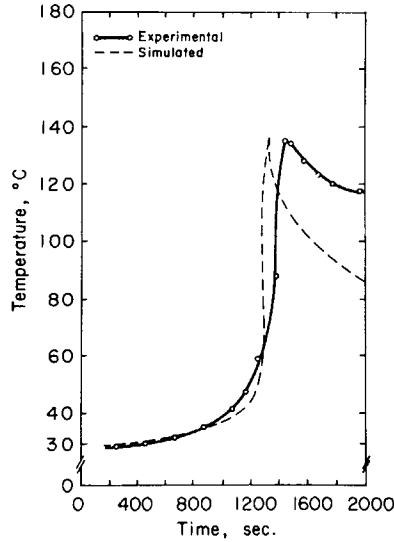
Fig. 7. Comparison of experimental (O——O) and simulated (- - -) temperature changes at the surface of the curing polymer (X = 0.0).
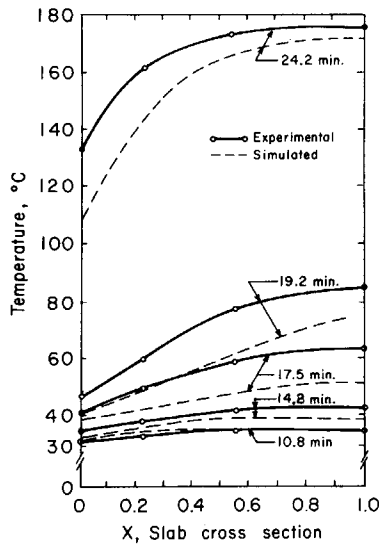

Fig. 8. Comparison of experimental (O——O) and simulated (- - -) temperature profiles in the curing polymer.

where

$$K' = \frac{Ah^2}{\alpha} e^{-B}$$

It was simply assumed that the rate of heat transfer from the polymer surfaces was proportional to the temperature difference across the mold walls. With this assumption, the boundary and initial conditions took the following form:

Initial conditions:

$$\theta(0,X) = 1$$

$$C(0,X) = 1$$

Boundary condition 1 (symmetry about $x = 0$):

$$\frac{\partial \theta}{\partial X} (\tau,0) = 0$$

$$\frac{\partial C}{\partial X} (\tau,0) = 0$$

Boundary condition 2 (mold wall):

$$\frac{\partial \theta}{\partial X} (\tau,1) = K[\theta(\tau,1) - \theta_a]$$

where K is an empirical constant and θ_a is the dimensionless ambient temperature.

Method of Solution

Equations (8) and (9) were solved simultaneously, subject to the boundary conditions, by a numerical technique. Since the two differential equations were coupled, an iterative procedure was followed. The basic numerical scheme involved the utilization of the Crank–Nicholson implicit finite difference method for the solution of the heat conduction equation and Euler's method for the solution of the reaction rate equation. The Crank–Nicholson implicit finite-difference approximation of eq. (8) is

$$-\frac{\lambda}{2} \theta_{i+1}^* + (F_i + \lambda)\theta_i^* - \frac{\lambda}{2} \theta_{i-1}^* = \frac{\lambda}{2} \theta_{i+1} + (F_i - \lambda)\theta_i + \frac{\lambda}{2} \theta_{i-1} + \phi_i \quad (11)$$

where

$$\lambda = \frac{\Delta\tau}{(\Delta X)^2}$$

$$F_i = 1 + aT_0(\theta_i - 1)$$

and

$$\phi_i = \Delta\tau K' \frac{\Delta H_R}{C_p^0 T_0 F_i} \left[1 - \frac{C_i^* + C_i}{2}\right]^{0.50} \left[\frac{C_i^* + C_i}{2}\right]^{1.50} \exp B \left[1 - \frac{2}{\theta_i^* + \theta_i}\right]$$

The asterisk denotes a value at the end of a time step, and the subscript i designates the grid point with x coordinate $i\Delta x$.

By applying eq. (10) to the grid points i = 2, ..., M and to the boundary conditions at $i = 1$, and at $i = M + 1$, the following tridiagonal system is obtained:

$$(F_1 + \lambda)\theta_1^* - \lambda\theta_2^* = (F_1 - \lambda)\theta_1 + \lambda\theta_2 + \phi_1 - \frac{\lambda}{2}\theta_{i-1}^* + (F_i + \lambda)\theta_i^*$$

$$-\frac{\lambda}{2}\theta_{i+1}^* = \frac{\lambda}{2}\theta_{i-1} + (F_i - \lambda)\theta_i + \frac{\lambda}{2}\theta_{i+1} + \phi_i$$

$$-\lambda\theta_M^* + [F_{M+1} + \lambda(1 + K\Delta X)]\theta_{M+1}^*$$
$$= \lambda\theta_M + [F_{M+1} - \lambda(1 + K\Delta X)]\theta_{M+1} + 2K\lambda\Delta X\theta_a + \phi_{M+1} \quad (12)$$

The tridiagonal system of equations thus obtained was solved simultaneously with the reaction rate equation. The reaction rate equation (in Euler's integration form) was

$$C_i^* = C_i + \frac{\Delta\tau}{2} Q_i [(1 - C_i)^{0.50} C_i^{1.50}] \tag{13}$$

where

$$Q_i = K' \exp B \left[1 - \frac{2}{\theta_i^* + \theta_i} \right]$$

Using a constant time increment throughout the complete polymerization reaction created some stability problems. It was necessary to use smaller values of the time increment where the reaction rate was changing rapidly. Twenty equal distance increments were used in $0 \leq X < 1$ ($M = 20$). Figure 2 shows the coordinate system of the castings. The complete FORTRAN program for the above calculations is available upon request.

RESULTS AND DISCUSSION

The output from the simulation gives the temperature and concentrations (here, extents of reaction) at 20 locations in the curing mass between its center line and its surface, at each time increment.

A common zero-time basis was selected in order to facilitate a comparison
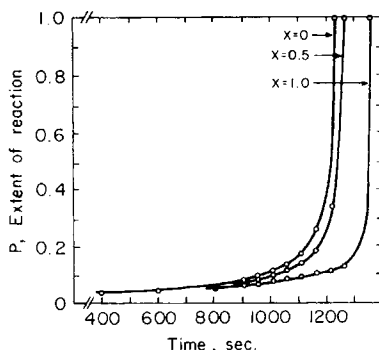

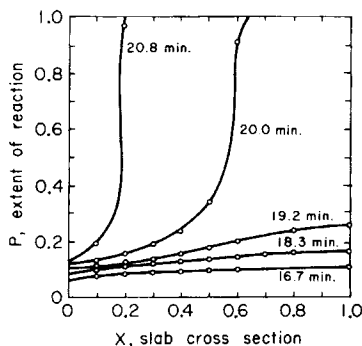Fig. 9. Extent of polymerization as function of time and position.

Fig. 10. Profiles of the extent of polymerization.

between the experimental and model-predicted temperature distributions. The time at which the thermocouple readings first showed a detectable temperature rise in the curing polymer mass was selected as the common "zero" of time, and the computer simulation was initiated using a uniform pouring temperature corresponding to these initial thermocouple readings. This gave more reproducible results than attempting to estimate the effective reaction starting time during the mixing and filling process. (The total cure time was about 22 min, and the total mixing and filling time was 110 sec.)

Simulated reaction exotherms at different locations within the polymer mass and temperature profiles at different times are shown in Figures 3 and 4. The agreement between these model-predicted and the experimental results (Figs. 5–8) is quite satisfactory over almost the entire reaction time interval. The accuracy of the simulation seems to be more dependent upon the values of the kinetic parameters than upon the thermal properties. Variations in thermal properties with cure had surprisingly little effect on the results; however, the process was simulated using the linear relations for heat capacity and conductivity determined earlier.[13] The density variation associated with shrinkage during cure had virtually no effect on the results, since it results in less than 3% change in linear dimension for maximum cure. The resulting compression of scale is of minor consequence when compared to the temperature rise in the curing casting. The shrinkage could be a significant factor for casting in rigid molds because this would result in separation of the casting from the mold surface, which would drastically affect the heat transfer. In this study, a flexible mold was used, and such separation was not observed. The simulated profiles could be improved by using a better relationship for the boundary condition at the mold wall, however.

To study the effect of heat conduction during curing, the model was also solved for an adiabatic boundary condition at the walls of the mold. Thus, the conduction term in the energy equation, eq. (5), was dropped, and the following equation resulted:

$$\frac{\partial T}{\partial t} = \frac{\Delta H_R}{C_p} A e^{-E_a/RT}(1 - C)^{0.50}C^{1.50} \tag{14}$$
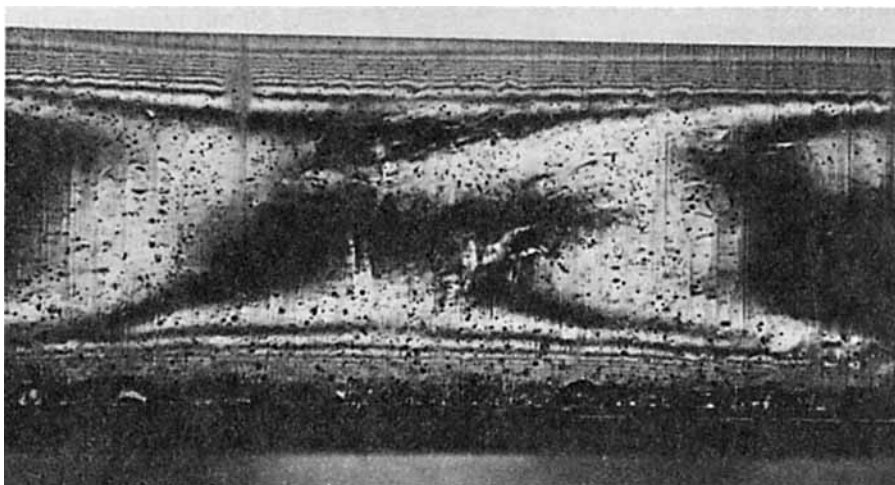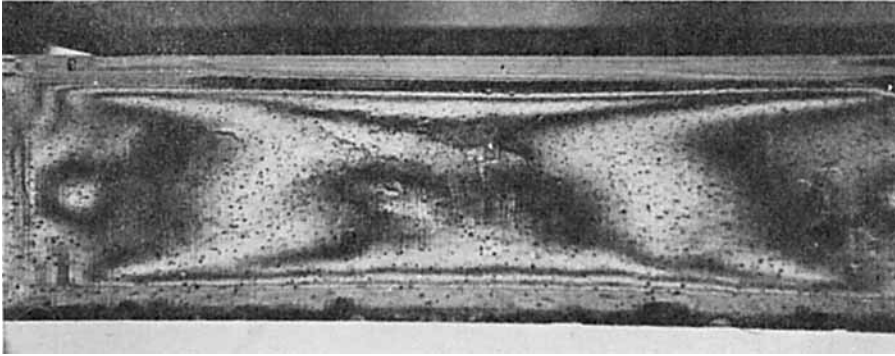

Fig. 11. Birefringence in sectioned cured polymer.

Fig. 12. Birefringence in sectioned cured polymer.

The predicted temperature rise in the curing mass for this case is shown in Figure 3. It is significant to note that even when heat conduction is included, the center of the slab had nearly an adiabatic rise. Only very near to the mold walls were the reaction exotherms reduced to less than the adiabatic rise. This was of course due to the increased effect of the heat transfer rate near the mold walls. Also, because of the poor conductivity of silicone rubber, the heat loss from the mold walls was not too large. This was clear from the nearly adiabatic character of the curing over a large section of the polymer mass. The variation of the extent of polymerization with time at different locations, and the profiles at different times during the reaction, are shown in Figures 9 and 10. It can be seen that the reaction was faster at the center and slower near the walls as a result of lower exotherms developed near the walls. That is, it took more time for the polymer near the surface to be cured.

Finally, the experimental castings were sectioned and the birefringent patterns in those pieces were visually observed using a polarscope. Typical results are shown in Figures 11 and 12. Each band (black and white) corresponds to the locus of points with a constant principal stress difference. The number of fringes increases near the polymer surfaces, which indicates the existence of residual stresses at those sections as a result of the temperature gradients developed during cure.

Nomenclature

T	temperature, K
T_0	initial polymer temperature, K
θ	dimensionless temperature
h	half slab thickness, cm
y	space variable, cm
X	dimensionless space variable
t	reaction time, sec
τ	dimensionless time
E_a	activation energy, cal/mole
α	thermal diffusivity, cm^2/sec
ΔH_R	total heat of reaction, cal/g
p	fraction of polymerized resin
ρ	density of resin, gm/cm^3
R	gas constant, 1.987 cal/g mole K

k_T thermal conductivity, cal/cm sec K

A frequency factor, sec^{-1}

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