

EFFECT OF KINETIC AND THERMAL PARAMETERS ON THE PROCESS OF CURE OF EPOXY RESIN IN A CYLINDRICAL MOULD

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Abstract—Various parameters were found to be important in the cure of epoxy resin, those concerned with the kinetics of the heat evolved from the reaction (such as the order, rate constant and activation energy) and those related to the thermal properties of the resin, such as thermal diffusivity and heat capacity. An important parameter in this case was also studied, viz. the coefficient of the heat transfer through the heated fluid–mould interface, controlled by convection. After modelling successfully the process with a numerical method with finite differences, each of the parameters was tested in turn, by considering the temperature and state of cure-history at the middle of the resin cured in a cylindrical mould. Some parameters were found to be significant in the cure, such as the cure enthalpy and heat capacity, the activation energy and the coefficient of heat transferred by convection. This new knowledge allowed further insight into the process of cure for thermosets.

LIST OF SYMBOLS

- α_s : sample diffusivity
 α_g : glass diffusivity
 λ_s : sample thermal conductivity
 λ_g : glass thermal conductivity
 C_s : sample specific heat
 C_g : glass specific heat
SOC: state of cure
 k_0 : rate constant of reaction
 E : activation energy
 ΔH : Q_∞ : enthalpy of cure reaction
 n : order of overall cure reaction
 MV : dimensionless number for the glass-mould
 $T_M = T_{\text{air}}$
 $\Delta T = T_M - T(NR + 2)$

INTRODUCTION

Epoxy resin sheet (or rod) moulding compound is one of a number of different materials which find various industrial applications. The requirements of these final materials are numerous, and include adequate strength and stiffness, with acceptable surface finish and good dimensional stability. All these characteristics are influenced by the processing method by which the final materials are made. The most important fact in this process is the highly exothermic reaction of cure coupled with a rather low thermal conductivity. As a result, the heat of cure can give rise to excessively high temperatures, especially at the middle of the sample, which may cause degradation of the material [1–4]. Moreover, substantial temperature gradients are developed within the sample [5–9] responsible for the development of other gradients of state of cure [7–9], and such effects can result in distortion of the mouldings.

The main purpose of this paper was to model the curing reaction of epoxy resin during the process in a long cylindrical mould. The aim was to predict both

the temperature–time profiles at any position within this cylinder and any time, and the state of cure–time profiles at the same place and time. The model described here was perfectly general and could be applied to moulding of any geometry [10–11]. However we considered only cylindrical samples with a length much greater than the radius. The mould described and used in this work was made of a thin wall heated by an external fluid. It was chosen and studied because it is particularly able to solve the two following problems of importance for epoxy resin: it can supply the resin with heat, and it can extract heat from the resin as fast as possible when necessary, by varying the temperature of the fluid.

An ultimate aim of the paper was to determine the effect of the various parameters of interest, those concerned with the thermal properties of the resin, such as thermal conductivity and heat capacity, and the coefficient of heat transfer at the fluid–mould interface, with the kinetics of the cure reaction. Some of the above parameters were found to be of importance for the cure of rubber [12–16].

The model used in the paper, based on a numerical method with finite differences, took into account not only the heat transferred by convection through the fluid–mould interface and by conduction through the mould and resin, but also the kinetics of the heat evolved from the cure reaction. The parameters of these kinetics were previously determined by calorimetry working either under isothermal conditions [7] or in the scanning mode [8–9].

THEORETICAL

In order to simplify the problem, some assumptions were made:

(i) The longitudinal heat transfer was neglected, the cylindrical sample being very long. Thus only the

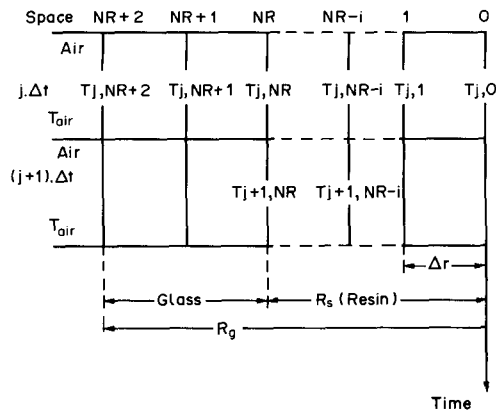


Fig. 1. Schematic diagram for numerical analysis.

radial heat transferred through the circular cross-section was considered.

(ii) Heat was transferred by conduction through the mould and resin. No matter transfer through the resin was taken into consideration.

(iii) Heat was transferred by free convection through the air-mould interface.

(iv) The rate of heat evolved from the cure reaction was expressed by a single Arrhenius equation, as determined by calorimetry.

(v) The state of cure was expressed by the extent of the internal heat evolved from the cure reaction (in %).

Mathematical treatment

The classical equation for heat transfer by radial conduction was reduced to:

$$\rho \cdot C \cdot \frac{\partial T}{\partial t} = \frac{1}{r} \cdot \frac{\partial}{\partial r} \left(r \cdot \lambda \cdot \frac{\partial T}{\partial r} \right) + \rho \cdot \frac{dQ}{dt} \quad (1)$$

by considering also the contribution of the heat of cure to the increase in temperature.

The rate of the heat of cure reaction was defined as a function of the total enthalpy Q_∞ by the following equation:

$$\frac{1}{Q_\infty} \cdot \frac{dQ_t}{dt} = k_0 \cdot \left(1 - \frac{Q_t}{Q_\infty} \right)^n \cdot \exp \left(-\frac{E}{RT} \right) \quad (2)$$

The problem had no analytical solutions, because of the two following facts: (i) the thermal parameters were temperature-dependent (ii) the presence of the internal heat generation from the cure reaction.

Numerical analysis

The problem studied in this work was solved by using an explicit numerical method with finite differences, this method being found to be suitable for micro-computers.

Equations available through the resin and mould

By considering the following circles of radius $(r - \Delta r)$, r , $(r + \Delta r)$ drawn through the circular cross-section, the heat balance written in the annulus

of internal radius $(r - \Delta r/2)$ and external radius $(r + \Delta r/2)$ allowed one to obtain:

$$\begin{aligned} & T(j+1, NR-i) \\ &= \frac{1}{MR} \cdot [T(j, NR-i-1) \\ &+ (NR-2) \cdot T(j, NR-i) \\ &+ (j, NR-i+1)] + \frac{1}{MR(NR-i)} \\ &\times [T(j, NR-i+1) - T(j, NR-i-1)] \\ &+ \frac{1}{C} \cdot \frac{dQ}{dt} \cdot \Delta t \end{aligned} \quad (3)$$

where $T(j, NR-i)$ was the temperature of the annulus between the radius $(NR-i-\frac{1}{2}) \cdot \Delta r$ and $(NR-i+\frac{1}{2}) \cdot \Delta r$ at the time $j \cdot \Delta t$.

The dimensionless number MR was expressed as a function of the increments of space Δr and time Δt .

$$MR = \frac{(\Delta r)^2}{\Delta t} \cdot \frac{\rho \cdot C}{\lambda} \quad \text{for the resin.} \quad (4)$$

Because of indetermination for $r=0$, another equation was needed for the middle of the resin.

$$\begin{aligned} T(j+1, 0) &= T(j, 0) + \frac{4}{MR} \cdot [T(j, 1) - T(j, 0)] \\ &+ \frac{1}{C} \cdot \frac{dQ}{dt} \cdot \Delta t. \end{aligned} \quad (5)$$

Equations available for the mould-resin interface

The heat balance written on the slices of resin and mould located on both sides of the mould-resin interface give the following result:

$$\begin{aligned} T(j+1, NR) &= T(j, NR) \\ &+ BV \cdot [T(j, NR+1) - T(j, NR)] \\ &- BR \cdot [T(j, NR) - T(j, NR-1)] \end{aligned} \quad (6)$$

where the coefficients BV and BR were found as follows:

$$BR = \frac{(2 \cdot R_s - \Delta r) \cdot \lambda_s \cdot \Delta t}{A \cdot (\Delta r)^2} \quad (7)$$

$$BV = \frac{(2 \cdot R_s + \Delta r) \cdot \lambda_g \cdot \Delta t}{A \cdot (\Delta r)^2} \quad (8)$$

with

$$A = \left(R_s + \frac{\Delta r}{4} \right) \cdot \frac{\lambda_g}{\alpha_g} + \left(R_s - \frac{\Delta r}{4} \right) \cdot \frac{\lambda_s}{\alpha_g} \quad (9)$$

Equations available for the air-mould interface

As the heat transfer through the air-mould interface was controlled by free convection, the following dimensionless numbers, Grashof and Prandtl, and Nusselt were used in order to obtain the coefficient of heat transfer h . This coefficient was expressed as a function of the size of the sample and the difference of temperature between the mould surface and air.

$$h = h_0 \cdot [TM - T(j, NR+2)]^{0.1} \quad (10)$$

where the constant h_0 depended on the radius of the cylinder.

The temperature of the surface of the mould was then obtained as follows:

Table 1. Value of parameters

Kinetics of reaction: $k_0 = 4 \times 10^{11}$ (per sec) $E = 27,140$ (cal/mol)	
$n = 1.5$ $\Delta H = 76$ cal/g	
Thermal parameters:	
Resin	$C_r = 0.2 + 0.003 \times T$ (cal/g·deg)
	$\lambda_r = 10^{-3}$ cal/cm·sec·deg
	$\alpha_r = 10^{-3}$ cal/cm ² (before T_{max})
	$\alpha_r = 6.5 \times 10^{-4}$ cal/cm ² (after T_{max})
Glass	$C_g = 0.3$ cal/g·deg
	$\lambda_g = 2.66 \times 10^{-3}$ (cal/cm·sec·deg)
	$\alpha_g = 4 \times 10^{-4}$ cal/cm ²
Coefficient of heat transfer:	
$h = 7.12 \times 10^{-4} \times \Delta T ^{0.156}$ (cal/cm ² ·sec·deg)	

$$T(j+1, NR+2) = T(j, NR+2) + h \cdot Z1 \times [TM - T(j, NR+2)] - Z2 \cdot [T(j, NR+2) - T(j, NR+1)] \quad (11)$$

with the coefficients $Z1$ and $Z2$:

$$Z1 = \frac{(2 \cdot R_g \cdot \Delta t \cdot \alpha_g)}{\left(R_g - \frac{\Delta r}{4}\right) \cdot \Delta r \cdot \lambda_g} \quad (12)$$

$$Z2 = \frac{(2R_g - \Delta r)}{\left(R_g - \frac{\Delta r}{4}\right) \cdot MV} \quad (12')$$

Calculation of the state of cure

The extent of the heat of cure and the state of cure, was calculated with the help of the recurrent relation:

$$\begin{aligned} \left(\frac{dQ}{dt}\right)_{j+1} \cdot \Delta t &= Q_{j+1} - Q_j \\ &= k_0(Q_{\infty} - Q_j)^n \cdot Q^{1-n} \cdot \left(\exp - \frac{E}{RT}\right) \end{aligned} \quad (13)$$

with

$$Q_j = \sum_{j=0}^j \left(\frac{dQ}{dt}\right)_j \cdot \Delta t \quad \text{and} \quad q_0 = 0.$$

The state of cure as described above, was obtained by the simple equation:

$$SOC_j = \frac{Q_j}{Q_{\infty}} \cdot 100. \quad (14)$$

EXPERIMENTAL

Materials and parameters

The resin used in this paper was obtained by mixing the epoxy resin (Lopox 200 from CDF-Chimie) and the hardener (D 2605 from CDF-Chimie) containing an anhydride of Me THP, and an accelerator with 0.75% of an aromatic amine (type A 105 from CDF-Chimie). The binary mixture was prepared at room temperature with continuous stirring, and then poured into the cylindrical glass-mould.

The best composition (in weight percent) was as follows [17]:

Epoxy resin: 55.6%
Hardener: 44.4%

The values of parameters are shown in Table 1, as obtained from experiments:

Mould and temperature measurements

The cylindrical glass-mould with the resin sample was put in an oven heated by air kept at constant temperature. A glass-mould of 1.5 cm diameter was used. The temperature was recorded at the middle of the resin sample, in the exterior air and on the exterior glass-mould surface.

RESULTS

Two results of interest are considered in this paper; viz. the temperature–time history and the state of cure–time history at the middle of the resin. The effect of the parameters on these profiles was studied by varying each parameter in turn and keeping the others constant.

Two kinds of parameters were considered; those concerned with the kinetics of the reaction and the enthalpy of cure and also those characterizing the thermal properties of the resin. Moreover, special attention was given to the coefficient of heat transfer for heat convection through the air–mould interface.

(1) Validity of the model

The temperature–time history (Fig. 2) was obtained from experiment and from calculation by using the model described above, when the radius of the cylinder was 1.5 cm. These results were in good agreement, proving the validity of the theoretical model, as well as the values determined for the kinetic and thermal parameters.

(2) Effect of the kinetics parameters

Four parameters were shown to be of interest for the cure of rubber [17], and they were worth attention for the cure of epoxy resin, especially the enthalpy of reaction because of its high value.

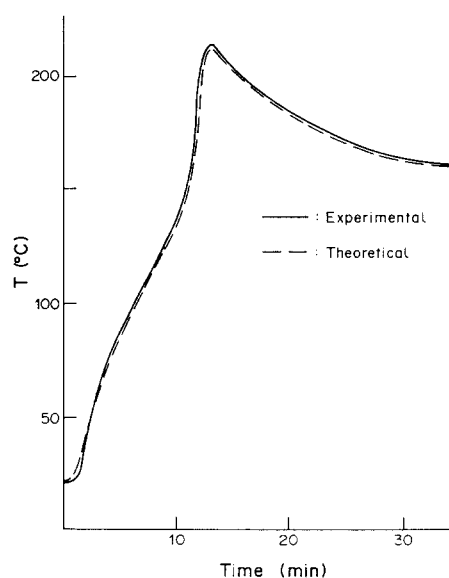


Fig. 2. Temperature–time history at the middle of the resin, proving the validity of the model for a diameter of 1.5 cm.

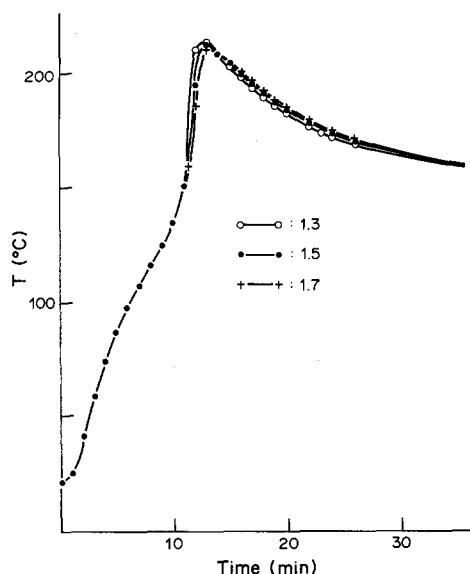


Fig. 3. Effect of the kinetic order on the temperature-time history at the middle of the resin: 1.3, 1.5, 1.7.

Effect of the order of the cure reaction. In a previous paper [18] on the cure in rubber sheets, the effect of the order on the rate of cure and the profiles of temperature was found to be negligible when the extent of cure was below 50%, but became increasingly greater when the extent of cure increased from 50 to 100%.

The profiles of temperature obtained at the middle of the resin, either from experiment and calculation for the order of 1.5, or from calculation for orders: 1.3 and 1.7, are shown in Fig. 3.

As a conclusion from these curves, the cure of epoxy resin came into line with the cure of rubber, the effect of the order on the profiles of temperature being very small.

Effect of a variation in the rate constant. The three values were chosen for the rate constant (3.2×10^{11} , 4×10^{11} and 4.8×10^{11} expressed in sec^{-1}) while the other parameters were kept constant. For each of these values, the profiles of temperature and state of cure were calculated, and the temperature-time and state of cure-time histories obtained at the middle of the resin are drawn in Fig. 4.

As shown in these figures, the effect of the rate constant on these profiles was of great importance, and some conclusions are worth noting.

(i) The higher the rate constant, the faster the cure reaction. This fact was responsible for a higher slope of the temperature-time history corresponding with the highest value for the rate constant. The change in the slopes of these curves appeared as soon as the reaction took place, around 120°C .

(ii) The maximum to which the temperature rose was higher when the highest value was used for the rate constant. The difference in these values was about 2°C .

(iii) Following the first conclusion, a higher value for the rate constant was accountable for an increase in the state of cure.

(iv) The state of cure-time curves were displaced along the time axis as shown in Fig. 4. An increase in 20% for the rate constant was followed by a reduction of about 40–45 sec in the time necessary for the state of cure to attain the same value, for instance 90%. These conclusions were previously reached for the cure of rubber [12, 16], but not in great detail.

Effect of variation in the activation energy. The effects of a slight variation in the activation energy of the cure reaction on the temperature-time and state of cure-time histories at the middle of the resin are shown in Fig. 5. The curves were calculated for values of E of 26,986, 27,140 and 27,330 cal/mol, while the other parameters were kept constant. These values were calculated by keeping $k_0 \cdot \exp(-E/RT)$ constant at the temperature of the mould, e.g. 150°C in the present case, while the rate constant was varied by 20% around the mean value obtained from experiment.

Of course, the lower the activation energy, the faster is the cure. Following this fact, the slopes of temperature-time history were found to be higher for the lower value of the activation energy. Moreover, a decrease in the activation energy reduced the time necessary for the SOC to attain the same value.

There is similarity between the curves drawn in Fig. 4 and Fig. 5 for the temperature-time histories, and the SOC-time histories. The point of importance for this parameter was the slight change in the activation energy, between 154 and 190 cal/mol, which was sufficient to cause the same effect as a variation of 20% in the rate constant.

Effect of the cure enthalpy. The mid-plane temperature increased to a maximum due to the internal reaction heat, which had adverse consequences on the properties of the final material, as already stated. The effect of the cure enthalpy on the temperature-time

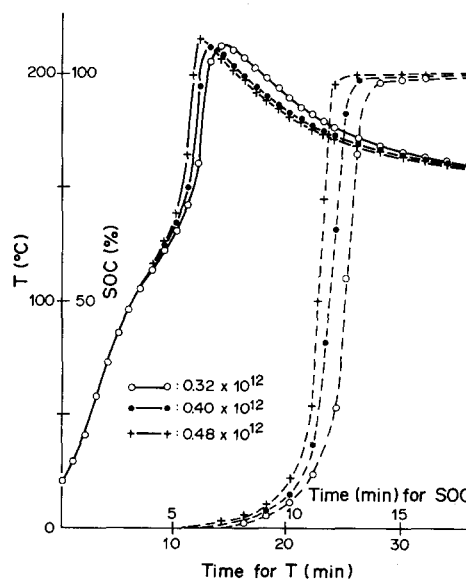


Fig. 4. Effect of the rate constant (sec^{-1}) on the temperature-time history (—) and on the SOC-time history (----) at the middle of the resin: 3.2×10^{11} , 4×10^{11} , 4.8×10^{11} .

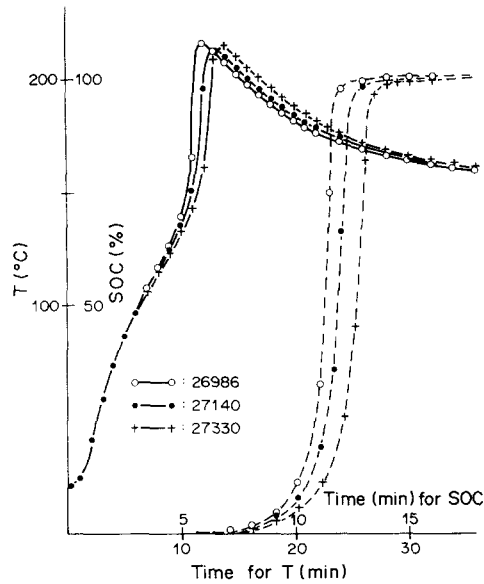


Fig. 5. Effect of the activation energy (cal/mol) on the temperature-time history (—) and on the SOC-time history (----) at the middle of the resin: 26,986, 27,140, 27,330.

profiles was very important, not only for the maximum values reached, but also for the slopes of these curves corresponding to the rate of heating, as shown in Fig. 6.

The effect of the cure enthalpy was not the same as the effect of the other kinetic parameters, the difference being essentially the change in the maximum value reached by the temperature. For instance, a variation of 20% in the cure enthalpy was re-

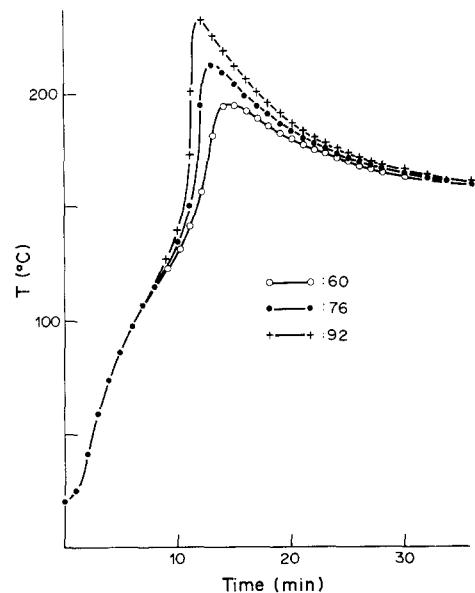


Fig. 6. Effect of the cure enthalpy (cal/mol) on the temperature-time history at the middle of the resin: 60, 76, 92.

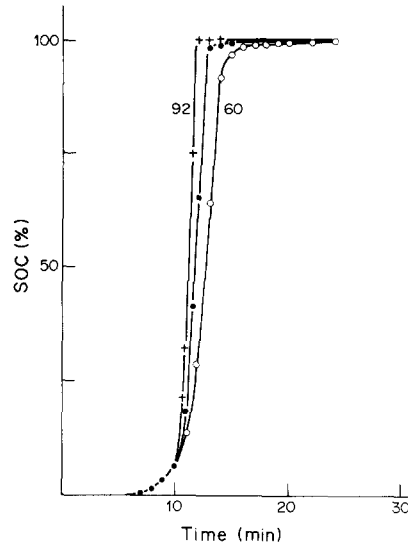


Fig. 7. Effect of the cure enthalpy (cal/mol) on the SOC-time history at the middle of the resin: symbols as in Fig. 6.

sponsible for a change in this temperature of about 18°C .

Following this fact, the effect of a variation in the cure enthalpy on the SOC-time history was very important, as shown in Fig. 7. These curves, obtained for the state of cure as a function of time, were quite different from the curves obtained in Figs 4 and 5 with the other kinetic parameters. Because of the high value of this parameter was more important than for rubber for which the enthalpy of cure is around 5 cal/g [15, 19].

(3) Effect of the thermal parameters of the resin

Two thermal properties were of interest for the resin, viz. the thermal conductivity and heat capacity. A previous paper concerned with rubber [13] showed that the effect of the thermal diffusivity was significant, without being very large.

We prefer here to distinguish between the effect of the thermal conductivity and heat capacity by varying them separately.

Effect of the thermal conductivity. The effect of this parameter was obtained by varying its value by 20% around the mean value obtained by experiment:

$$C = 0.2 + 0.003 \times T$$

by keeping constant the heat capacity and density of the resin. The final result can be seen in Fig. 8 for the temperature-time profiles and for the SOC-time profiles obtained by calculation.

Some conclusions can be drawn: (i) The effect of the thermal diffusivity was not very large. (ii) The effect on the profiles was found to be apparent not only during the cure, but also during the periods of heating and cooling of the resin. (iii) The curves in Fig. 8 could be obtained by translation along the time axis, a higher thermal conductivity allowing a higher value for the temperature and state of cure at the same time.

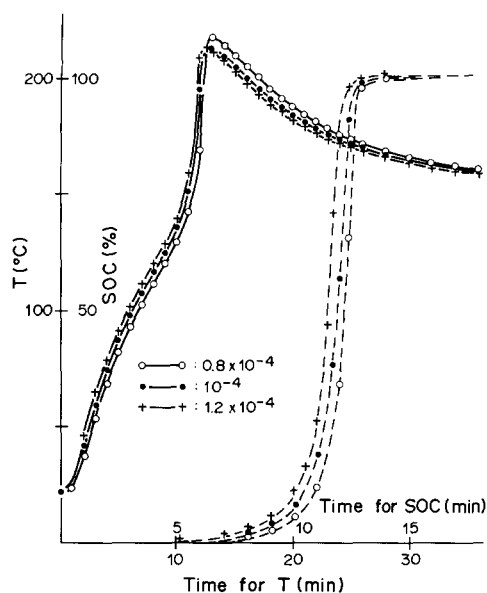


Fig. 8. Effect of the thermal conductivity (cal/cm \cdot sec \cdot deg) on the temperature-time history (—) and on the SOC-time history (---) at the middle of the resin: 0.8×10^{-4} , 1×10^{-4} , 1.2×10^{-4} .

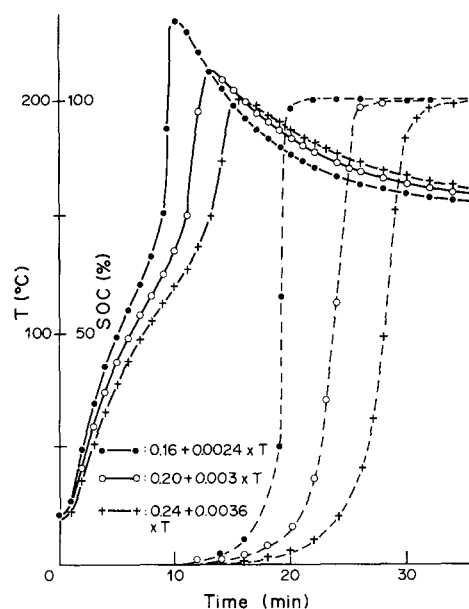


Fig. 9. Effect of the heat capacity (cal/g \cdot deg) on the temperature-time history (—) and on the SOC-time history (---) at the middle of the resin: $0.16 + 0.0024 \times T$, $0.2 + 0.003 \times T$, $0.24 + 0.0036 \times T$.

Effect of heat capacity of the resin. Although a thermal property of the resin in the same way as the thermal conductivity, the heating capacity did not play the same role as the other parameter. By referring to Eqn 1, we can see that the thermal diffusivity was acting upon the heat transfer by conduction, while the heat capacity was intervening on both the conduction heat and the internal heat generated from the cure.

The effect of the heat capacity of the resin on the temperature-time history was calculated by varying the value of the heat capacity by 20% around the mean value obtained from experiment. As heat capacity was found to be a function of temperature (Table 1), we varied both coefficients thus: $(0.16 + 0.024 \times T)$, $(0.2 + 0.03 \times T)$ and $(0.24 + 0.036 \times T)$.

As shown in Fig. 9, the effect of the heat capacity on the temperature-time history was found to be very important. As this parameter was acting on both the conduction heat and the internal heat of cure, the effect was particularly complicated. On the one hand, heat capacity was acting in an inversely proportional way to the enthalpy of cure; on the other hand, it was inversely proportional to the thermal diffusivity. These effects were superimposed as can be seen by comparing the curves in Figs 6, 8 and 9.

The effect of heat capacity on the SOC-time history was found to be very important, following the preceding effect on the temperature (Fig. 9).

(4) Effect of the coefficient of heat transfer

The coefficient of heat transfer, characterizing the intensity of the heat transferred by convection through the air-mould interface, was an important parameter, especially for this kind of mould.

Three values for this coefficient, obtained by varying by 20% around the mean experimental value

(5.9×10^{-4} , 7.12×10^{-4} and 8.54×10^{-4}) were tested. As shown in Fig. 10 for the temperature-time history obtained with these values for the coefficient h , the effect of the coefficient of heat transferred by convection was very important and of great interest. This coefficient had also a significant effect on the SOC-time history, an increase in its value causing a decrease in the time of cure by around 15% (Fig. 10).

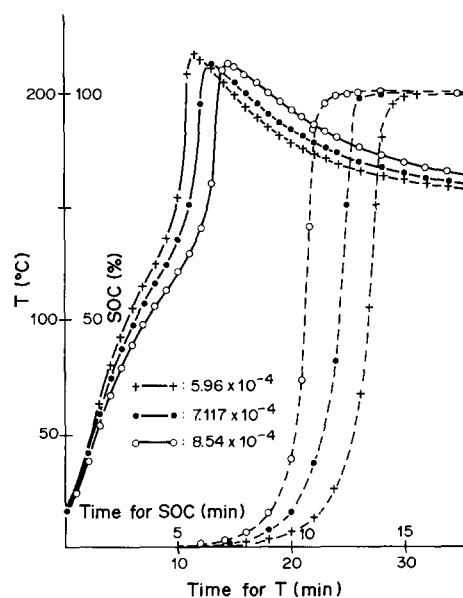


Fig. 10. Effect of the coefficient of heat transferred by convection ($\times 10^4$ cal/cm 2 \cdot sec \cdot deg) on the temperature-time history (—) and on the SOC-time history (---) at the middle of the resin: 5.96×10^{-4} , 7.12×10^{-4} , 8.54×10^{-4} .

CONCLUSIONS

Because of the various parameters playing a role in the cure of epoxy resin, it was necessary to determine the effect of each of these factors. In order to gain a fuller insight on the cure process of thermosets, this work was devoted to the study of the effects of all these parameters on the temperature and time-histories obtained by calculation at the middle of the resin cured in a cylindrical mould.

Each parameter was separately studied in turn. As a result, they could be put in three classes: the first with the parameters concerned with the kinetic parameters of the cure reaction, such as the order, rate constant, activation energy and the cure enthalpy; the second with the thermal properties of the resin, such as the thermal diffusivity and heat capacity; a special parameter was also studied, concerned with the nature of the heat transfer through the heated fluid-mould interface controlled by convection.

Some parameters were found to play an important role on the development of the cure, especially the cure enthalpy and heat capacity, the activation energy, and the coefficient of heat transfer by convection. We could understand after this study the need to have accurate experimental values for these parameters.

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