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REGULATION OF THE PROCESS OF CURE OF THERMOSETS BY VARYING THE COEFFICIENT OF SURFACE HEAT TRANSFER

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Abstract—Because of the high exothermicity of the cure reaction of thermosets associated with their low thermal conductivity, large increases in temperature within the material are observed with steep gradients of temperature. In order to reduce the increase in temperature and steep gradients, a new procedure is examined, by varying the coefficient of heat transfer on the surface of the mould and the resin. This change in this coefficient is obtained by varying the rate of stirring of the oil which heats the mould, and by keeping the oil temperature constant. This method is capable of reducing the increase in temperature within the resin, without increasing the time of cure significantly.

NOMENCLATURE

C_n = Specific heat capacity for the sample at position n,
C_m = constant specific heat capacity for the mould,
E = activation energy,
k_0 = rate constant of reaction,
MR, M_m = dimensionless numbers for the sample and for the mould,
n = integer indicating the position,
N_r, N_m = number of slices in the half-sample, in one slab of the mould,
p = order of overall cure reaction,
Q_i, Q_∞ = heat evolved from reaction up to time $t = i \cdot \Delta t$, enthalpy of reaction,
SOC = state of cure,
$T(n)$, $TN(n)$ = temperature in the place n, at time t and $t + \Delta t$, respectively,
Δt = finite increment of time,
ΔT = $T(\text{oil}) - T(\text{NT})$,
Δx_m, Δx_r = finite increment of space in the mould and the sample,
λ_m, λ_r = thermal conductivity for the mould and for the sample,
ρ_m, ρ_r = density for the mould and for the sample.

INTRODUCTION

Understanding and predicting the cure process of thermosetting materials is of practical interest both in the materials manufacturing process and the end-product performance. The most important aspect in the cure of thermosets is the highly exothermic nature of the cure reaction, which is associated with a rather low thermal conductivity of the resin either in the liquid or the solid state. As a result, steep temperature gradients are developed within the resin while the cure enthalpy gives rise to large increase in temperature. This heterogeneity during the process for temperature, and subsequently for the state of cure within the bulk of the resin, may be responsible for distortion of thin flat panels [1–4] and even for discoloration of the surface.

Unfortunately, the process of cure is quite complex for thermosetting materials, because of two main facts which act simultaneously, viz. heat transfer through the resin and the mould by conduction, with a coefficient of heat transfer onto the surface of the mould, and the internal heat evolved by the cure reaction. Instead the rule of thumb which have been widely used in the industry for curing rubbers [5–7], models of the process are capable of describing the process in a quantitative way. Numerical models taking into account all the known facts have been successfully tested in many cases for thermosetting resins [8–13]. These studies were carried out when the resin, located in a glass mould, was heating either in air or in oil. Other numerical models were developed in the interesting case of a metallic mould heated by oil, this mould being capable of working with a wide range of thicknesses of the resin sheet [14]. The effect of the temperature of the oil on the rate of cure proved to be of special interest [15]. Another parameter, with the coefficient of surface heat transfer at the oil–mould interface was also considered [16], by using either motionless oil or oil with various rates of stirring. The numerical model was also tested in the case of dissipation of heat generated by the reaction, by varying the temperature of the oil during the cure [17].

The main purpose of this paper is to develop a new way for dissipating part of the heat generated by the reaction without lengthening the time of cure cycle, and thus for reducing the steep gradients developed within the resin. The method consists of varying the coefficient of surface heat transfer at the oil–mould interface, by modifying the rate of stirring of the oil which is kept at constant temperature.

The kinetics of heat evolution from the overall curing reaction is determined by calorimetry working in the scanning mode. As the resin consists of a

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mixture, rather large samples are used in the calorimeter in order to have a sample representative of the homogeneity of the batch from which it is extracted, while the heating rate is low enough [18, 19].

EXPERIMENTAL PROCEDURES

Materials

The composite selected for the study was of the type "Bulk moulding compound" (Menzolit). It consists of the following components: (in w/w%).

Maleic polyester resin	16%
Vinyl acetate	10.7%
Hydrated alumina	66.7%
Magnesia	0.1%
Catalyst	0.5%
Styrene	4.1%
Zinc stearate	1.9%
	100%
Fibreglass	20%

All the components were intimately mixed, and the glass fibres were added and dispersed in the viscous mixture.

Moulding and heating system [14–16]

The composite was placed in the metallic mould, and pressed into the mould slabs. A thin thermocouple was set at the middle of the sample. The dimensions of the sample and mould were:

sample thickness: 0.7 cm
mould thickness: 0.38 cm
sample diameter: 3.4 cm

The mould with the sample in it was introduced into the silicone oil kept at constant temperature (146°), with a controlled rate of stirring. The temperature at the middle of the resin was recorded during the process.

Kinetic and thermal parameters

The kinetic parameters were determined by calorimetry working in the scanning mode (DSC 111, SETARAM, France) at a heating rate of 0.5°/min. Rather large samples of around 0.15 g were used because of the heterogeneity of the composite. The kinetic parameters were calculated from the heat flux–temperature curves by various methods [18, 19].

THEORETICAL

Before developing the mathematical treatment as well as the numerical analysis, it is necessary to present the assumptions. The following assumptions are made in order to set up the problem and to clarify the process.

Assumptions

- (i) Only one dimensional heat transfer is considered in spite of the fact that the sample is cylindrical in shape, because the thickness is much smaller than the diameter.
- (ii) Heat is transferred by a three-stage process: heat convection through the oil onto the mould surface with the coefficient of heat transfer h. Heat conduction within the mould, as well as within the resin.
- (iii) Heat convection at the oil–mould interface is either free (or natural) when the oil is motionless, or forced when the oil is stirred.
- (iv) The rate of generation of internal heat from the overall cure reaction is expressed in terms of temperature by an Arrhenius equation, with a single activation energy.
- (v) The thermal parameters of the resin vary either with temperature or with the value of the state of cure. The thermal conductivity varies with the state of cure in a discontinuous way, while heat capacity increases linearly with temperature.
- (vi) Perfect contact between the resin and mould exists at the interface.

Mathematical treatment

The equation of heat transfer by conduction in one-dimension with a cure reaction is expressed by:

$$\rho \cdot C \cdot \frac{\partial T}{\partial t} = \frac{\partial}{\partial x}\left(\lambda \cdot \frac{\partial T}{\partial x}\right) + \rho \cdot \frac{\partial Q}{\partial t} \tag{1}$$

where contributions to the increase in temperature due to heat conduction and heat evolved from the cure reaction are written in succession in the right hand term.

The rate of heat generated by the overall cure reaction is expressed in terms of temperature by an Arrhenius equation, and is also proportional to the partial enthalpy not yet evolved after time t:

$$\frac{1}{Q_\infty} \cdot \frac{\mathrm{d}Q_t}{\mathrm{d}t} = k_0 \left(1 - \frac{Q_t}{Q_\infty}\right)^p \cdot \exp\left(-\frac{E}{RT}\right). \tag{2}$$

Numerical analysis

No analytical expression can be found for the problem because of the internal heat generated by the reaction and by the state of cure dependence of the thermal conductivity. The problem is thus solved by using an explicit numerical method with finite differences. The thickness of the material is divided into slices of fixed thickness both for the resin and for the mould. Because of the midplane of the resin which is a plane of symmetry, there are $2N_r$ slices in the resin

Table 1. Thermal and kinetic parameters

Composite	$p = 2.3$	$k_0 = 9 \times 10^{21}$/sec	$E = 43{,}350$ cal/mol
	$\rho = 1.77$ g/cm^3	$C_p = 0.27 + 10^{-4} \cdot T$ (°C) cal/g·deg	
	$\Delta H = 18$ cal/g		
	$\lambda = 1.9 \times 10^{-3}$ cal/sec·cm·deg when SOC < 75		
	$\lambda = 3.3 \times 10^{-3}$ cal/sec·cm·deg when SOC > 75		
Mould (Duralumin)		$\rho = 2.7$ g/cm^3	
	$C_p = 0.22$ cal/g·deg	$\lambda = 0.296$ cal/cm·sec·deg	
Coefficient of surface heat transfer (cal/cm^2·sec·deg)			
	without motion of oil:	$h = h_0 \cdot \Delta T^{0.25}$ and $h_0 = 2 \times 10^{-3}$	
	with motion	$H = 8 \times 10^{-3}$	

and N_m slices through the thickness of each metallic slab of the mould. The midplane of each slice is associated with an integer (Fig. 1). From the heat balance evaluated within a slice during the increment of time Δt by considering in the composite transient heat conduction as well as internal heat generated by the cure reaction, and in the mould transient heat conduction only, the new temperature after time Δt is expressed in terms of the previous temperatures obtained at the same place and adjacent two places.

Composite, with $0 \leqslant n \leqslant N_r - 1$

The new temperature TN_n is given by:

$$TN_n = \frac{1}{MR_n}[T_{n+1} + (MR_n - 1)T_n + T_{n-1}] + \frac{\Delta Q_n}{C_n} \quad (3)$$

where T_n is the previous temperature at position n, and ΔQ represents the amount of heat evolved from the cure reaction within the slice of midplane n during the time Δt (per unit mass of resin).

The dimensionless number MR_n in the resin is:

$$MR_n = \frac{(\Delta x_r)^2}{\Delta t} \cdot \left(\frac{\rho \cdot C_n}{\lambda}\right)_r \quad (4)$$

Mould, with $N_r + 1 \leqslant n \leqslant N_m + N_r - 1$

The new temperature in the mould is:

$$TN_n = \frac{1}{M_m}[T_{n+1} + (M_m - 2)T_n + T_{n+1}] \quad (5)$$

with the dimensionless number M_m for the mould:

$$M_m = \frac{(\Delta x_m)^2}{\Delta t} \cdot \left(\frac{\rho \cdot C}{\lambda}\right)_m . \quad (6)$$

Composite–mould interface, with $n = N_r$

Two half slices are considered on each side of the composite–mould interface. The heat balance is evaluated during the time increment Δt within these two half slices, by considering heat conduction in the mould and the resin as well as heat evolved from the cure reaction in the resin. As the resin and mould are assumed to be in perfect contact, the temperature is the same on each side of the interface.

The new temperature TN_{N_r} at the interface is thus expressed in terms of the previous temperatures at the interface and at the adjacent places in the resin and the mould.

$$TN_{N_r} = A \cdot T_{N_r+1} + (1 - A - B) \cdot T_{N_r} + B \cdot T_{N_r-1} + \frac{D}{4}(3\Delta Q_{N_r} + \Delta Q_{N_r-1}) \quad (7)$$

where the coefficients are as follows:

$$A = \frac{\Delta t}{F} \cdot \left(\frac{\lambda}{\Delta x}\right)_m \quad B = \frac{\Delta t}{F} \cdot \left(\frac{\lambda}{\Delta x}\right)_r$$

$$D = \frac{(\rho \cdot \Delta x)_r}{2F} \quad F = \frac{(\rho \cdot C \cdot \Delta x)_m}{2} + \frac{(\rho \cdot C \cdot \Delta x)_r}{2} \quad (8)$$

Mould–oil interface

The heat balance during the increment of time Δt is evaluated within half the slice of the mould located next to the mould–oil interface, by considering the heat conduction through the mould and heat convection from oil to the mould surface.

The new temperature at the mould–oil interface TN_{N_m} is given by:

$$TN_{N_m} = \frac{1}{M_m}[2T_{N_m-1} + (M_m - 2N - 2) \times T_{N_m} + 2N \cdot T_{oil}] \quad (9)$$

where TN_{N_m-1} is the temperature in the mould at position N_{m-1} and T_{oil} is the temperature of the oil.

M_m and N are the dimensionless numbers

$$N = h \cdot \left(\frac{\Delta x}{\lambda}\right)_m \quad (10)$$

where h is the coefficient of convection heat transfer. This coefficient h is expressed by:

$h = 2 \times 10^{-3} \times \Delta T^{0.25}$ with motionless oil

$h = 8 \times 10^{-3}$ cal(cm$^2 \cdot$sec$\cdot$deg) with stirred oil.

Conditions of stability for calculation

The coefficients given for calculating the previous temperature must be such that:

$$MR > 2 \quad M_m > 2$$
$$M_m - 2N - 2 > 2 \quad 1 - A - B > 0. \quad (11)$$

State of cure

The state of cure (SOC) is given by:

$$\mathrm{SOC} = 100\frac{Q_t}{Q_\infty} = 100 \cdot Y_t . \quad (12)$$

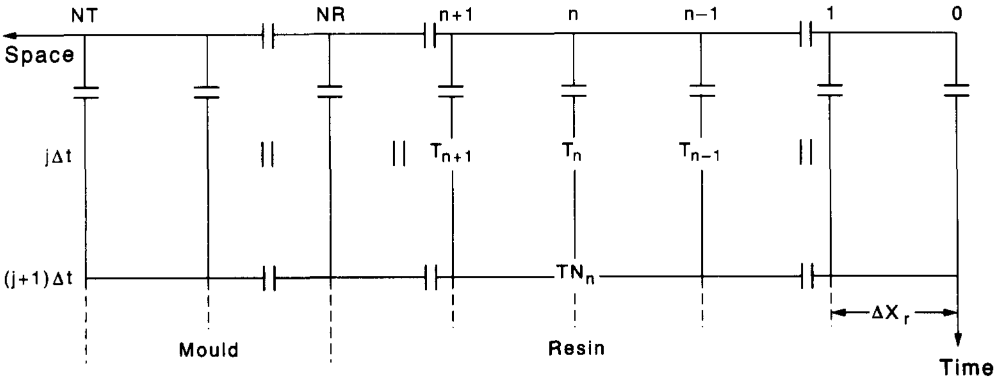

Fig. 1. Space–time diagram for numerical analysis.

Upon putting the function S_t

$$S_t = k_0 \int_0^t \exp\left(-\frac{E}{RT_\theta}\right)\cdot d\theta \tag{13}$$

$$\text{with } 0 \leqslant \theta \leqslant t \tag{14}$$

there is:

$$S_{t+\Delta t} = S_t + k_0 \cdot \Delta t \cdot \exp\left(-\frac{E}{RT_t}\right) \tag{15}$$

with

$$S_0 = 0 \tag{16}$$

and Y_t can be obtained by integration of equation (2) at the constant temperature T_t.

$$Y_t = 1 - [1 + (p-1)S_t]^{1/1-p}. \tag{17}$$

The amount of heat generated by the reaction during the interval Δt, from time t to $(t + \Delta t)$ is thus expressed by:

$$\Delta Q = Q_\infty \cdot (Y_{t+\Delta t} - Y_t). \tag{18}$$

RESULTS

Two results are of interest, one concerned with the validity of the model, the other with the effect of the change in the rate of stirring of oil during the process and thus of the change in the value of the coefficient of surface heat transfer.

1. Validity of the model

The validity of the model is tested by comparing the temperature–time histories at the midplane of the resin obtained either by experiment or by calculation. As shown in an earlier paper [14], the temperature–time history at the midplane of the resin is determined with good accuracy because, the midplane being a plane of symmetry, the gradient of temperature is always zero at this place, and a slight change in the position of the thermocouple alters only slightly the value of the temperature measured.

Two temperature–time histories at the midplane are drawn (Fig. 2), one being obtained without stirring [1], the other with a controlled rate of stirring [2] for which $h = 8 \times 10^{-3}$ cal/cm^2·sec·deg. The experimental and calculated temperature–time histories are very well superimposed in these two cases, proving the validity of the model.

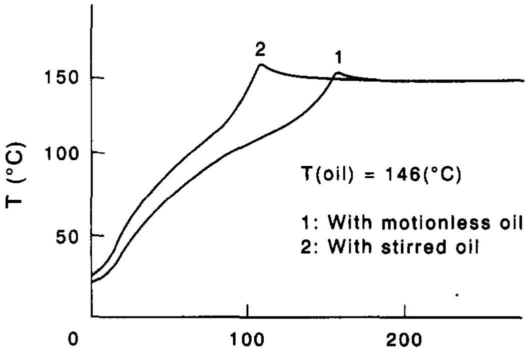

Fig. 2. Temperature–time histories at the middle of the thin sheet of resin, with oil at 146°. 1, With motionless oil; 2, with stirred oil at a given rate.

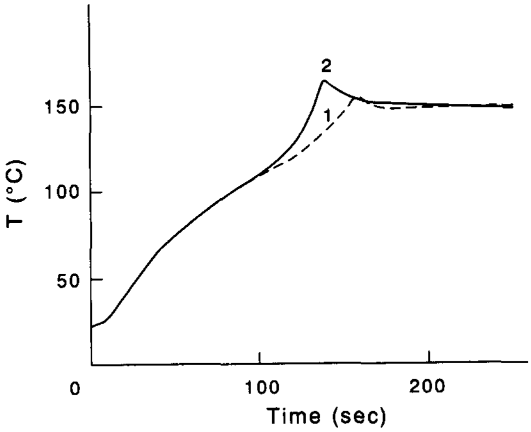

Fig. 3. Temperature–time histories at the midplane of the sheet. 1, With motionless oil, 2, with motionless oil at times lower than 85 sec and stirred oil at time higher than 85 sec.

Two results are worth noting:

(i) The process is well described by the numerical model either when the oil is motionless or stirred.

(ii) The temperature–time histories at the midplane are quite different when the oil is in motion or not. The coefficient of surface heat transfer is higher when the oil is stirred than when it is motionless. As a result, the two curves are quite different throughout.

(iii) Three stages can be considered in the process: a stage of heating up to a temperature around 100°; a stage of cure, after an inflection point in the temperature–time history; a stage during which the temperature is constant and equal to the temperature of the mould.

(iv) A maximum is observed in the temperature–time history at the midplane. The position of this maximum strongly depends on the stirring of the oil. Of course, this temperature maximum is higher and obtained at a shorter time when the oil is stirred than when it is motionless.

2. Effect of the change in the rate of stirring on the temperature–time histories

The principle of the method developed here is as follows: the sample with the mould is introduced into the oil bath kept at constant temperature and at a given rate of stirring. After a given time, the rate of stirring of the oil is changed to another given rate.

Two examples are considered: one, when the sample and mould are immersed in motionless oil, and the oil is stirred during the process. The other, when the sample and mould are placed in the oil with a given rate of stirring, and the stirring is stopped during the process (Fig. 4).

The temperature–time histories at the midplane in these two cases are shown in: Fig. 3, where the history obtained by increasing the rate of stirring is drawn with the history measured and calculated with

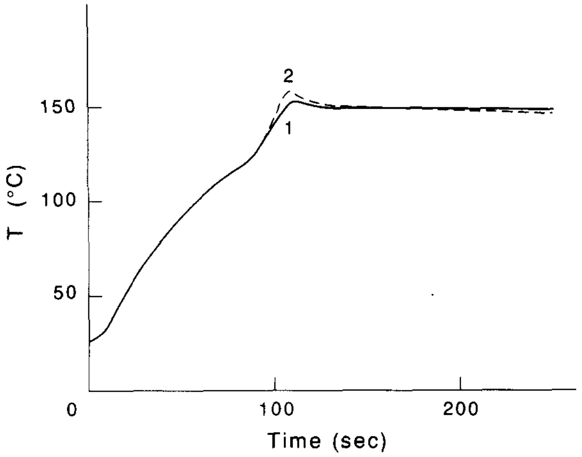

Fig. 4. Temperature–time histories at the midplane, of the sheet. 1, With stirred oil at times lower than 85 sec and motionless oil at times higher than 85 sec; 2, with stirred oil.

motionless oil. Figure 4, where the history determined by stopping the stirring during the process is compared with the history obtained with the constant rate of stirring shown in Fig. 2 curve 2.

The following conclusions can be drawn:

(i) In Fig. 3, the two temperature–time histories at the midplane of the resin are obtained when the oil was motionless at the beginning of the process. At a given time (85 sec), the stirring of oil is established at a constant rate very quickly [2]. This time is selected because it corresponds to an inflection point due to the beginning of the cure reaction at the midplane of the resin.

(ii) Of course, these two temperature–time histories are the same up to the time at which the stirring is established.

(iii) After the time at which the stirring of oil is established in one case [2], the temperature–time histories diverge. The rate of cure is higher and the maximum is attained at a shorter time when the oil is in motion.

(iv) Of course, the increase in the stirring is responsible for an increase in the coefficient of surface heat transfer.

(v) In Fig. 4, the two samples are immersed in stirred oil at the beginning, and the heating stage is the same in curves 1 and 2.

(vi) In Fig. 4, the rate of heat evolved by the cure reaction is reduced by stopping the stirring of oil. The maximum of temperature at the midplane is thus significantly reduced (153 instead of 158°).

(vii) A comparison between the maximum of the temperatures at the midplane shown in the curves 2 in Fig. 3 and 4 is of interest. The temperature is higher in Fig. 3 where the oil is first motionless and then stirred.

3. Effect of the stirring of oil on the profiles of temperature and SOC within the sample

The profiles of temperature developed through the thickness of the sample, as well as the profiles of the state of cure are of great interest, enabling one to obtain a fuller insight of the process.

These profiles of temperature and state of cure are calculated with the numerical model in various cases:

In Fig. 5, when the oil is motionless during the whole process

In Fig. 6, when the oil is stirred during the whole process

In Fig. 7, when the oil is firstly motionless, and then stirred after a time of 85 sec.

In Fig. 8, when the oil is stirred at the beginning, and then is motionless after 85 sec.

The following results from these curves are pointed out:

(i) Steep profiles of temperature are developed through the thickness of the sample. At the beginning of the process, during the heating stage, the temperature is higher on the surface than at the midplane. During the cure stage, other gradients are developed,

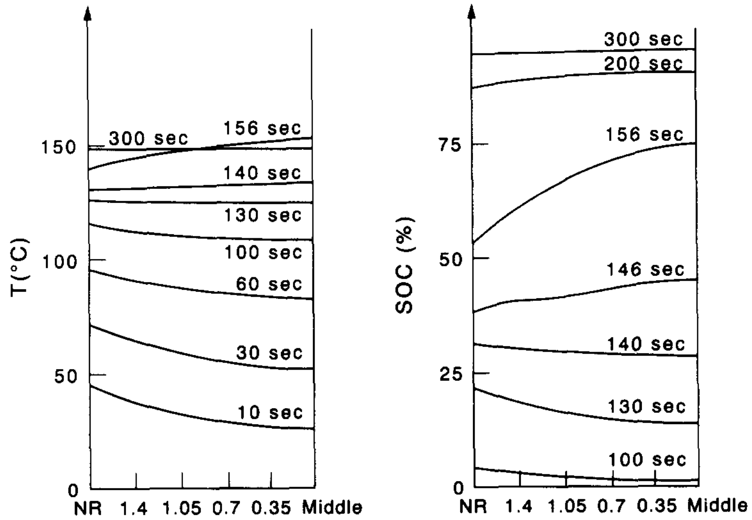

Fig. 5. Profiles of temperature (left) and state of cure (right), when the oil is stirred during the whole process, at 146°.

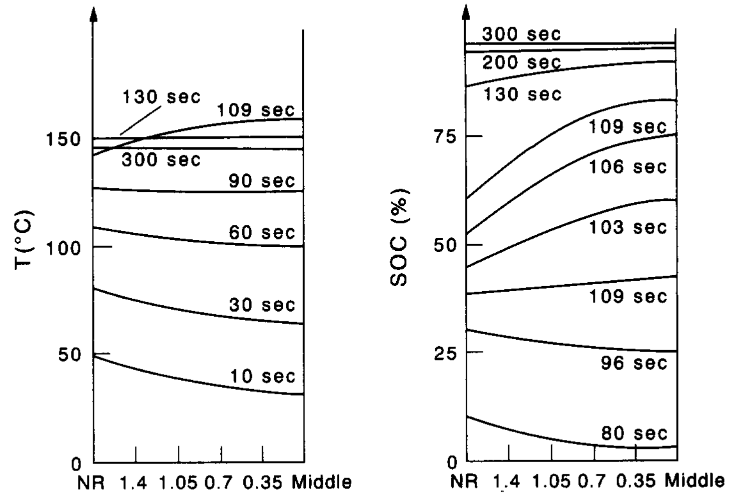

Fig. 6. Profiles of temperature (left) and state of cure (right), when the oil is stirred during the whole process, at 146°.

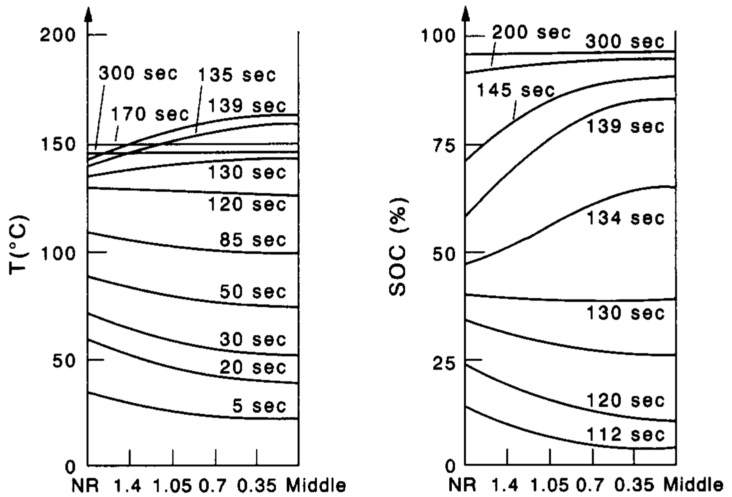

Fig. 7. Profiles of temperature (left) and state of cure (right), when the oil is motionless, at $t < 85$ sec, then stirred at $t > 85$ sec, at 146°.

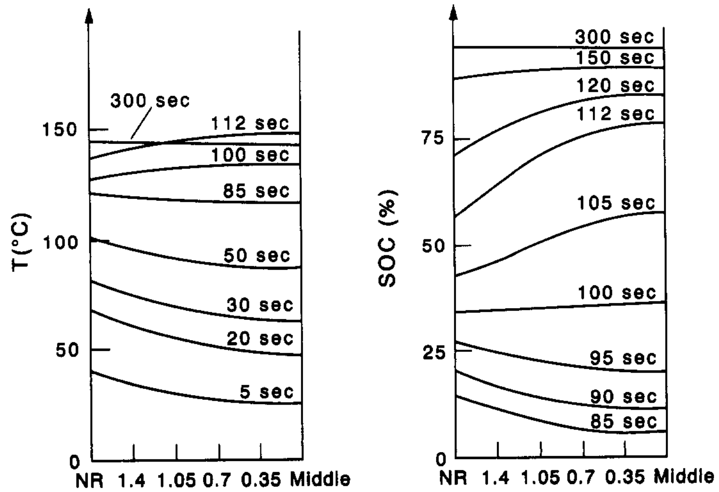

Fig. 8. Profiles of temperature (left) and state of cure (right), when the oil is stirred at $t < 85$ sec, and motionless at $t > 85$ sec, at 146°.

and a higher temperature is observed at the midplane. This fact is especially significant at the maximum of the temperature–time history at the midplane. After this maximum, the gradients of temperature become flatter and flatter.

(ii) Steep profiles of state of cure are also developed through the thickness of the sample. During the first stage of heating, the state of cure is higher on the surface than at the midplane. During the stage of cure, because of the internal heat of reaction, the state of cure is higher at the midplane, and the steepest gradient is obtained at the maximum of the temperature–time history at the midplane. Heterogeneity in the material is thus created during the cure, by considering the temperature and especially the state of cure.

(iii) Comparison between the profiles of temperature and state shown in Fig. 5 without stirring and in Fig. 6 with stirring of oil is very informative. Steep gradients of temperature and state of cure develop in these two cases, but the time of cure is shorter when the oil is stirred and the coefficient of surface heat transfer is greater.

(iv) The effect of the increase in stirring on the process is clearly shown by comparing Figs 5 and 7 when the oil is initially motionless, and the effect of the decrease in stirring is also shown by comparing the Figs 6 and 8 when the oil is initially stirred.

(v) The process of heating starting with stirred oil and followed by motionless oil is responsible for a decrease in the value of the temperature at the maximum of the temperature–time history at the midplane of the resin.

CONCLUSIONS

Because of the high exothermicity of the cure reaction of thermosets associated with a low thermal conductivity, large gradients of temperature and subsequently steep gradients of state of cure are developed within the resin during the curing process. A problem of interest is to reduce these steep gradients as well as the increase in temperature in the resin, in order to obtain final materials with better properties.

A new method consisting of varying the coefficient of surface heat transfer onto the surface of the mould is studied in this paper. This change in the coefficient of heat transfer is obtained by varying the rate of stirring, as this coefficient of heat transfer increases with the rate of stirring. Two particular cases are considered: one of these is of special interest, when the heated oil is stirred at the beginning of the immersion of the mould and the resin, and then is motionless at a given time. The gradients of temperature and state of cure are not so steep and the increase in termperature in the resin is significantly reduced.

Modelling the process with the help of a numerical method with finite differences is capable of bringing complementary information to experiments, and thus gaining fuller insight into the nature of the process.

REFERENCES

1. S. Y. Pusatcioglu, J. C. Hassler, A. L. Frickle and H. A. McGee. *J. appl. Polym. Sci.* **25,** 381 (1980).
2. R. C. Progelhof and J. L. Throne. *Polym. Engng Sci.* **15,** 690 (1975).
3. P. K. Mallik and N. Raghupathi. *Polym. Engng Sci.* **19,** 774 (1979).
4. R. M. Barone and D. A. Caulk. *Int. J. Heat Mass Transfer* **22,** 1021 (1979).
5. H. S. Y. Hisch. *J. appl. Polym. Sci.* **27,** 3265 (1982).
6. R. W. Wise. *Rubber Technology* (edited by M. Morton), Chap. 4. Van Nostrand–Reinhold, New York (1973).
7. J. P. Ryne. Proceed. of RAPRA Seminar, Shawbury, May (1979).
8. J. A. Nixon and J. M. Hutchinson. *Plast. Rubber Process Applic.* **5,** 349 (1985).
9. M. Chater, J. Bouzon and J. M. Vergnaud. *Plast. Rubber Process Applic.* **7,** 199 (1987).
10. M. Chater and J. M. Vergnaud. *Eur. Polym. J.* **24,** 245 (1988)
11. M. Chater and J. M. Vergnaud. *J. Polym. Engng* **8,** 1 (1988).
12. A. El Brouzi, R. Granger, J. Brouzon and J. M. Vergnaud. *Plast. Rubber Process Applic.* **12,** 7 (1989).
13. M. Chater and J. M. Vergnaud. *Eur. Polym. J.* **7,** 563 (1987).
14. K. Azaar, A. El Brouzi, R. Granger and J. M. Vergnaud. *Eur. Polym. J.* **27,** 1431 (1991).
15. K. Azaar, A. El Brouzi, R. Granger and J. M. Vergnaud. *J. Polym. Engng* (in press).
16. K. Azaar, A. El Brouzi, R. Granger and J. M. Vergnaud. *Plast. Rubber Composites, Process Applic.* (in press).
17. A. El Brouzi, J. Brouzon and J. M. Vergnaud. *Plast. Rubber Process Applic.* **14,** 101 (1990).
18. H. Liu, J. Y. Armand, J. Bouzon and J. M. Vergnaud. *Thermochim. Acta* **126,** 81 (1988).
19. J. Y. Armand and J. M. Vergnaud. *Thermochim. Acta* **131,** 15 (1988).