Thermochimica Acta, 228 (1993) 83–93
Elsevier Science Publishers B.V., Amsterdam

The effect of thermal parameters on the cure of a bulk moulding composite with polyester

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(Received 16 March 1993; accepted 2 April 1993)

Abstract

Because composites made of polyester are transformed into three dimensional solid materials during the irreversible cure reaction, a good knowledge of this process is advantageous. The effect of the thermal parameters such as the thermal conductivity and heat capacity of the resin on the process are of great interest. Heat capacity plays an important role because it influences both the heat transferred by conduction and the heat evolved by the cure reaction. Thermal conductivity influences heat conduction alone, and thus is less important. The kinetics of the heat generated by the cure reaction were determined by calorimetry in scanning mode. The study was carried out using a thin sheet of composite heated into the slabs of a mould, with a one-dimensional heat transfer. A numerical model that had been previously tested, provided the precise effect of each parameter on the process.

LIST OF SYMBOLS

C_p	specific heat capacity for the composite at position p
C_m	constant specific heat capacity for the mould
E_a	activation energy
k_0	pre-exponential factor
n	order of the overall reaction,
R	universal gas constant
MR_p, MM_m, A, B, N	dimensionless numbers defined in eqns. (4), (6), (8) and (10), respectively
D, F	numbers defined in eqn. (8)
p	integer indicating the position
N_r, N_m	number of intervals in the half-sample and in one slab of the mould, respectively
N_t	$N_r + N_m$
Q_i, Q_∞	heat evolved from reaction up to time $t = i\Delta t$, enthalpy of reaction per unit mass

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S_i	function defined in eqn. (13)
SOC	state of cure
HF	heat flux
T_p, TN_p	temperature at position p, at times t and $t + \Delta t$, respectively,
T_{oil}	temperature of heating oil
Δt	finite time increment
Δx_{m}, Δx_{r}	finite increments of space in the mould and the sample
h	coefficient of surface heat transfer
λ_{m}, λ_{r}	thermal conductivity of the mould and the sample
ρ_{m}, ρ_{r}	density of the mould and the sample

INTRODUCTION

Because thermosetting resins are transformed into a three-dimensional network during curing following an irreversible reaction, it is important to have a good understanding of this process. Bulk moulding composites are generally pressed into a mould and heated up to a temperature at which the reaction develops; the shape of the final material is given by the mould. Two facts are relevant to the cure reaction: firstly, the high exothermicity of the reaction and the sensitivity of the rate of reaction to temperature, and secondly, the rather low thermal conductivity of the uncured and cured resin. As a result of this high exothermicity associated with a low thermal conductivity, large increases in temperature appears, especially in the middle of the composite, and steep temperature gradient occur throughout the material [1–4]. These facts are generally responsible for the discoloration and degradation of the composite as well as the distortion of the moulding [5–8].

Therefore, studies have been made to attempt to control the reaction and to reduce both the increase in temperature and temperature gradients. Excess heat may be extracted from the composite and mould during the cure either by altering the temperature of the mould which can be varied during the process [3], or by altering the heat exchanged between the mould and heating system by varying the coefficient of surface heat transfer [4]. The effect of the operational conditions on the cure process is very important, and a slight change in temperature may disturb the characteristics of the final material. In all cases, a good knowledge of the process is required, and a numerical model that can describe the process is very helpful.

The main purpose of this paper is to determine the effect of the thermal parameters on the cure process. Because the composite is made of unsaturated polyester with fibres and various loads and additives, it is rather heterogeneous, and the determination of the kinetics and thermal parameters is rather complex. The kinetic parameters were obtained from calorimetric measurements made in scanning mode, using a rather large sample and a subsequent low heating rate. The small sample taken from the bulk of the resin may be considered as representative of the homogeneity of the batch [9–11]. The measurement of thermal parameters generally suffers from a lack of accuracy, and this is especially true for composites.

In order to make the problem manageable, a previously tested numerical model was used. This model considers all the known conditions, namely heat conduction through the mould and composite with good contact at the interface, heat convection at the external surface of the mould, and internal heat generated by the cure reaction [3, 4, 9, 12, 13]. The results are generally expressed by the changes in temperature and state of cure with time, obtained from samples taken from the middle of the sheet [9, 12]. They can also be illustrated in a better way by considering the heat flux at a given place, particularly at the composite–mould interface [14].

THEORETICAL

The following assumptions are made in order to clarify the problem.

(i) A thin sheet of composite is used and one-dimensional heat conduction is considered.

(ii) The rate of heat evolved from the overall cure reaction is expressed by an Arrhenius equation, with constant parameters.

(iii) The sheet of composite is pressed between the slabs of a metallic mould heated by forced convection in oil stirred at a given rate.

Mathematical treatment

The equation of heat conduction in one dimension with internal heat of cure reaction is

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

where the contributions of heat conduction and exothermic reaction are on the right-hand side.

The rate of heat evolved from the overall cure reaction is expressed as a function of the partial enthalpy evolved up to time t by

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

where n is the order of the reaction, E_a the activation energy, and k_0 a pre-exponential factor.

Numerical analysis

The analytical treatment of the problem with the above two equations is not feasible [9], and a numerical model is used.

The principle of the method is summarized as follows. The thickness of the mould and composite are divided into N_m and $2N_r$ slices of constant width Δx_m and Δx_r. The new temperature after an elapse of time Δt, TNp, is expressed in terms of the previous temperatures at the same and adjacent places, by evaluating the heat balance within the slice. Various places are considered associated with the integer p.

Within the composite, with $0 \leq p < N_r$

The new temperature in the composite is

$$TN_p = \frac{1}{MR_p}[T_{p+1} + (MR_p - 1)T_p + T_{p-1}] + \frac{\Delta Q_p}{C_p} \tag{3}$$

with the dimensionless quantity MR_p

$$MR_p = \frac{(\Delta x_r)^2}{\Delta t}\left(\frac{\rho C_p}{\lambda}\right)_r \tag{4}$$

where ΔQ_p is the amount of heat evolved from the cure reaction per unit mass during the increment of time Δt at position p.

Within the mould, with $N_r + 1 \leq p \leq N_t - 1$

$$TN_p = \frac{1}{MM_m}[T_{p+1} + (MM_m - 2)T_p + T_{p-1}] \tag{5}$$

with $N_t = N_r + N_m$ and the dimensionless number MM_m

$$MM_m = \frac{(\Delta x_m)^2}{\Delta t}\left(\frac{\rho C}{\lambda}\right)_m \tag{6}$$

Composite–mould interface, with $p = N_r$

Because good contact is maintained between the composite and mould, the temperature at the interface TN_{int} is given by [3, 4]

$$TN_{int} = AT_{int+1} + (1 - A - B)T_{int} + BT_{int-1} + \frac{D}{4}(3\Delta Q_{int} + \Delta Q_{int-1}) \tag{7}$$

with the coefficients

$$A = \frac{\Delta t}{F}\left(\frac{\lambda}{\Delta x}\right)_m \qquad B = \frac{\Delta t}{F}\left(\frac{\lambda}{\Delta x}\right)_r \qquad D = \frac{(\rho \Delta x)_r}{2F} \tag{8}$$

$$F = \tfrac{1}{2}[(\rho C \Delta x)_m + (\rho C \Delta x)_r]$$

Mould–oil interface, with $p = N_t$

The heat balance during the increment of time Δt is evaluated within the slice of thickness $\Delta x_m/2$ in the mould next to the surface by accounting for heat conduction through the mould and heat convection onto the mould surface. The new temperature at the mould surface TN_{surf} is thus expressed in terms of the previous temperature on this surface and at the next slice in the mould by

$$TN_{\mathrm{surf}} = \frac{1}{MM_{\mathrm{m}}}[2T_{\mathrm{surf}-1} + (MM_{\mathrm{m}} - 2N - 2)T_{\mathrm{surf}} + 2NT_{\mathrm{oil}}] \tag{9}$$

where T_{surf} is the temperature in the mould at position N_{t-1}, and T_{oil} is the temperature of the oil, with the dimensionless number N

$$N = h\left(\frac{\Delta x}{\lambda}\right)_{\mathrm{m}} \tag{10}$$

where h is the coefficient of surface heat transfer by forced convection.

Conditions of stability for calculation

The coefficient of the previous temperature in various places must be positive, yielding the conditions

$$MR_p > 2 \qquad M_{\mathrm{m}} > 2 \qquad M_{\mathrm{m}} - 2N > 2 \qquad 1 - A - B > 0 \tag{11}$$

State of cure in the resin

Putting

$$S_i = k_0\int_0^{i\Delta t} \exp\left(-\frac{E_{\mathrm{a}}}{RT_t}\right) \mathrm{d}t \tag{12}$$

the term S_{i+1} can be evaluated as

$$S_{i+1} = S_i + k_0\,\Delta t \exp\left(-\frac{E_{\mathrm{a}}}{RT_i}\right) \tag{13}$$

with

$$S_0 = 0 \tag{14}$$

The heat generated by the cure reaction up to time t is given by

$$\frac{Q_i}{Q_\infty} = 1 - [1 + (n-1)S_i]^{1/(1-n)} \tag{15}$$

when n is different from unity.

EXPERIMENTAL

Materials

The composite used was a bulk moulding compound (BMC from Menzolit). It consists of a maleic polyester resin (16%), styrene (4.1%), catalyst (0.5%), vinyl acetate (10.7%), hydrated alumina (66.7%), magnesia (0.1%) and zinc stearate (1.9%). Fibreglass (20 parts) is dispersed in the above mixture (100 parts).

Kinetic and thermal parameters

The kinetic parameters of the cure reaction were determined from the heat flux–temperature curves obtained by calorimetry in scanning mode. A rather large sample (150 mg) was used with the calorimeter (DSC 111, Setaram) because of the heterogeneity of the composite, while the heating rate was low (2°C min^{-1}). The kinetic parameters obtained were tested by superimposing the heat flux–temperature curves obtained by calculation and from experiments [9–11].

The coefficient of surface heat transfer was determined by fitting the experimental and calculated temperature–time histories from samples in the middle of the cured composite. The thermal parameters were taken from the literature. The values are shown in Table 1.

TABLE 1

Kinetic and thermal parameters

Composite:	$k_0 = 9 \times 10^{21}\ \text{s}^{-1}$; $E_a = 181.2\ \text{kJ mol}^{-1}$; $p = 2.3$; $Q = 75.2\ \text{kJ kg}^{-1}$; $\rho = 1770\ \text{kg m}^{-3}$; $C = 1.13 + 4.18 \times 10^{-4} \times T(°\text{C})\ \text{kJ kg}^{-1}\ \text{K}^{-1}$; $\lambda = 1.00\ \text{W m}^{-1}\ \text{K}^{-1}$, for $\text{SOC} < \text{SOC}_{\text{MAX}}$; $\lambda = 1.38\ \text{W m}^{-1}\ \text{K}^{-1}$ for $\text{SOC} > \text{SOC}_{\text{MAX}}$.
Duralumin mould:	Thickness = 3.8 mm; $\rho = 2700\ \text{kg m}^{-3}$; $C = 0.92\ \text{kJ kg}^{-1}\ \text{K}^{-1}$; $\lambda = 123.7\ \text{W m}^{-1}\ \text{K}^{-1}$.
Coefficient of surface heat transfer by forced convection $h = 334\ \text{W m}^{-2}\ \text{K}^{-1}$	

RESULTS

The effect of the thermal parameters, namely the thermal conductivity λ and heat capacity C of the composite, on the process is evaluated by varying each of these parameters around their mean value. Two results are considered: one with the temperature–time and state-of-cure–time histories obtained from the middle of the composite; and the other with the heat flux calculated at the composite–mould interface.

The temperature–time history in the centre of the composite is of interest for at least two reasons: being a plane of symmetry, the derivative of temperaure with respect to space at this position is zero, and a slight change in position of the thermocouple does not result in great change in the temperature measurement; there is a greater change in temperature at this position [3, 4, 12, 14]. Of course, there is a drawback in this kind of measurement because the sample is destroyed [14].

The heat flux at the composite–mould interface, however, involves a non-destructive measurement, because the heat flux-meter can be placed on the surface of the mould in the same way as for a calorimeter [14].

The effect of the thermal conductivity of the composite

The effect of the thermal conductivity of the composite on the process was determined by using the model and varying the values of the thermal conductivity by 10% around the mean value. As shown in eqn. (1), the thermal conductivity influences only the heat conduction.

The temperature–time histories at the mid-plane are shown in Fig. 1, the state-of-cure–time histories at the mid-plane are shown in Fig. 2, and the heat flux at the composite–mould interface in Fig. 3.

Some conclusions can be drawn from these figures.

(i) A change of 10% around the mean value of the thermal conductivity is responsible for a significant change in the temperature–time history at the mid-plane, and an appreciable change in the state-of-cure–time history and the heat flux–time history at the composite–mould interface.

(ii) At the beginning of the process, during the heating stage up to around 106 s, a lower thermal conductivity produces a retardation in heating and the temperature–time curve is shifted to higher times in Fig. 1. A similar result is observed for the state-of-cure–time history in Fig. 2.

(iii) Throughout the cure, and especially at the maximum reached by the temperature at the middle of the composite (Fig. 1), a lower thermal

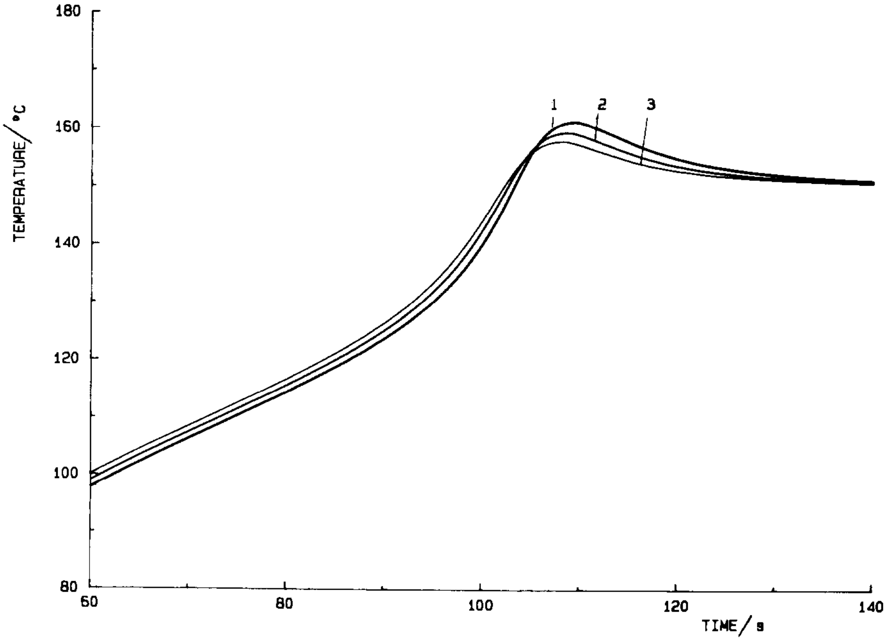

Fig. 1. Temperature–time histories at the middle of the composite for various values of the thermal conductivity of the composite: curve 1, $\lambda_1 = 0.9$, $\lambda_2 = 1.24\ \mathrm{W\,m^{-1}\,K^{-1}}$; curve 2, $\lambda_1 = 1.0$, $\lambda_2 = 1.38\ \mathrm{W\,m^{-1}\,K^{-1}}$; curve 3, $\lambda_1 = 1.1$, $\lambda_2 = 1.52\ \mathrm{W\,m^{-1}\,K^{-1}}$.

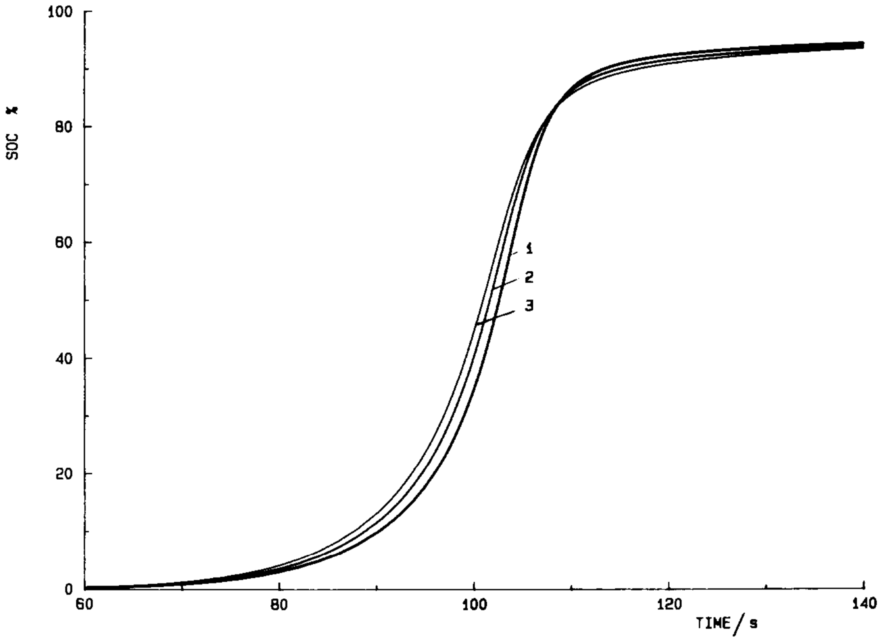

Fig. 2. State-of-cure-time histories at the middle of the composite for various values of the thermal conductivity of the composite: curve 1, $\lambda_1 = 0.9$, $\lambda_2 = 1.24$ W m^{-1} K^{-1}; curve 2, $\lambda_1 = 1.0$, $\lambda_2 = 1.38$ W m^{-1} K^{-1}; curve 3, $\lambda_1 = 1.1$, $\lambda_2 = 1.52$ W m^{-1} K^{-1}.

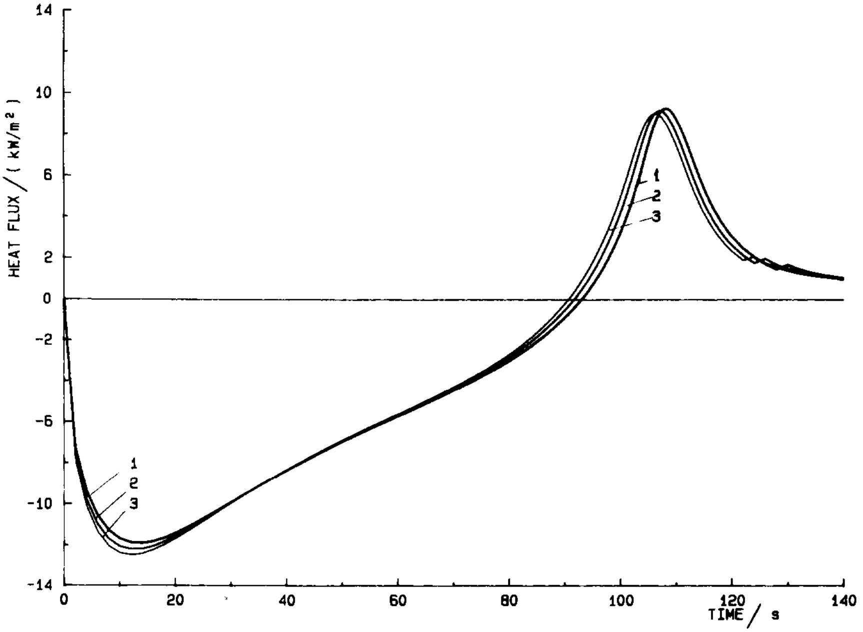

Fig. 3. Heat flux-time historis at the composite-mould interface for various vaues of the thermal conductivity of the composite: curve 1, $\lambda_1 = 0.9$, $\lambda_2 = 1.24$ W m^{-1} K^{-1}; curve 2, $\lambda_1 = 1.0$, $\lambda_2 = 1.38$ W m^{-1} K^{-1}; curve 3, $\lambda_1 = 1.1$, $\lambda_2 = 1.52$ W m^{-1} K^{-1}.

conductivity is associated with a higher value of this maximum in temperature.

Effect of heat capacity of the composite

The heat capacity influences not only the heat conduction but also the heat generated by the cure reaction, as shown in eqn. (1). The effect of heat capacity on the cure process is determined by varying the value given to this parameter in the model. Three types of results are presented: the temperature–time history (Fig. 4) and the state-of-cure–time history obtained in the middle of the composite (Fig. 5); and the heat flux–time history at the composite–mould interface (Fig. 6). Remembering that the temperature change of a material is inversely proportional to the heat capacity, the following observations can be made.

(i) A lower heat capacity results in a faster rate of heating during the heating stage, when heat conduction alone is acting, and a higher maximum temperature obtained at a shorter time (Fig. 4).

(ii) Following the above results, a lower heat capacity is associated with a faster rate of cure, as shown in Fig. 5. It may be noticed that the three curves drawn in this figure are virtually parallel.

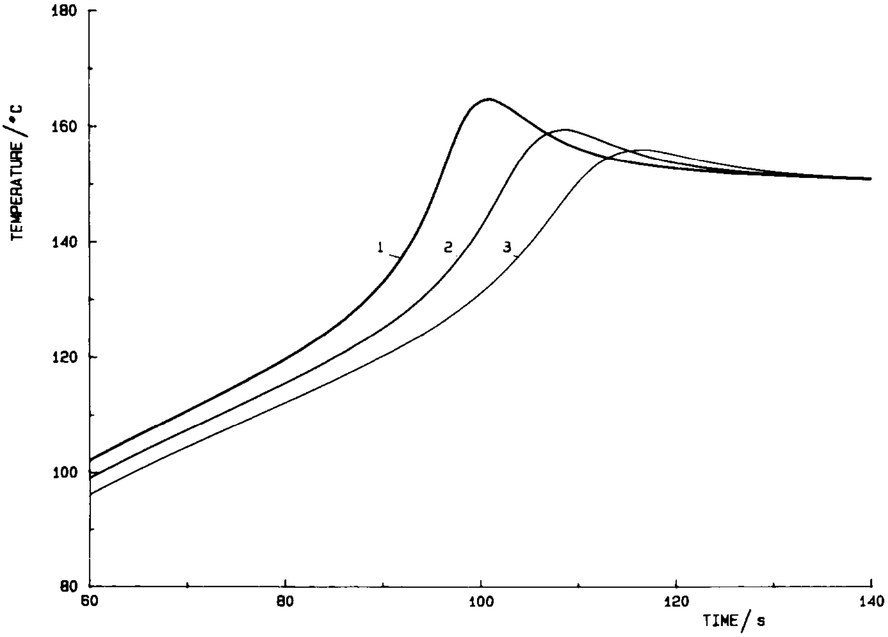

Fig. 4. Temperature–time histories at the middle of the composite for various values of the heat capacity of the composite: curve 1, $C = 1.017 + 3.76 \times 10^{-4} \times T(°C)$ kJ Kg^{-1} K^{-1}; curve 2, $C = 1.130 + 4.18 \times 10^{-4} \times T(°C)$ kJ kg^{-1} K^{-1}; curve 3, $C = 1.243 + 4.60 \times 10^{-4} \times T(°C)$ kJ kg^{-1} K^{-1}.

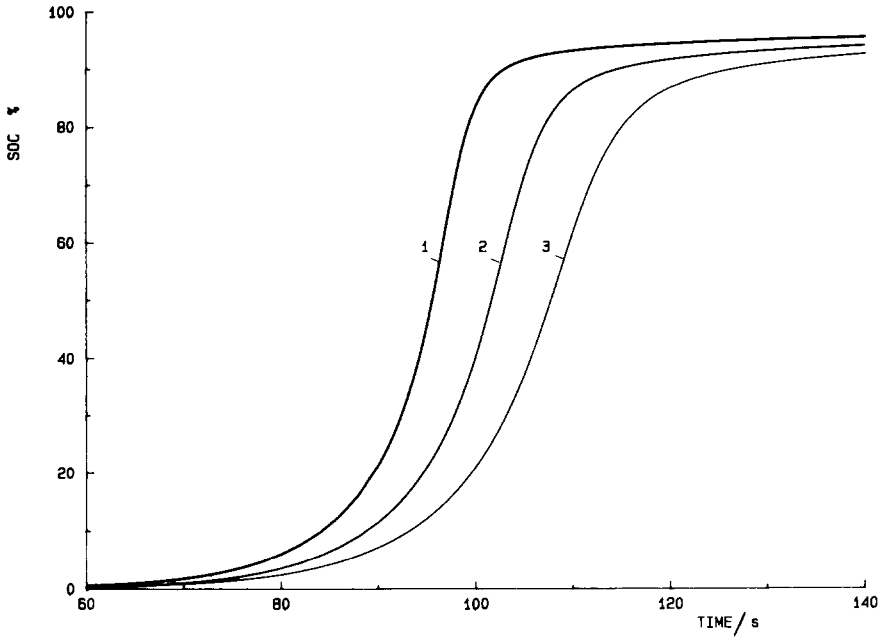

Fig. 5. State-of-cure–time histories at the middle of the composite for various values of the heat capacity of the composite: curve 1, $C = 1.017 + 3.76 \times 10^{-4} \times T(°C)$ kJ kg^{-1} K^{-1}; curve 2, $C = 1.130 + 4.18 \times 10^{-4} \times T(°C)$ kJ kg^{-1} K^{-1}; curve 3, $C = 1.243 + 4.60 \times 10^{-4} \times T(°C)$ kJ kg^{-1} K^{-1}.

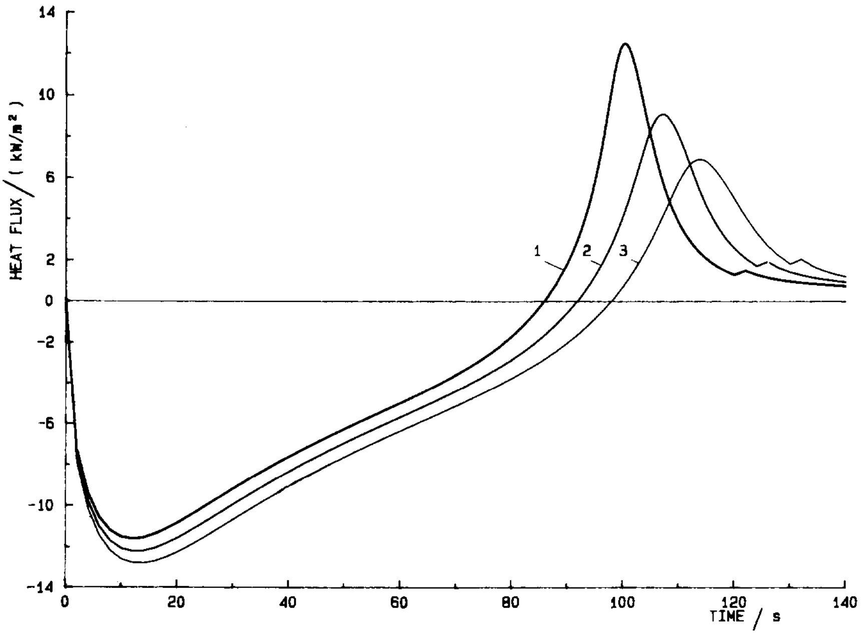

Fig. 6. Heat flux–time histories at the composite–mould interface for various values of the heat capacity of the composite: curve 1, $C = 1.017 + 3.76 \times 10^{-4} \times T(°C)$ kJ kg^{-1} K^{-1}; curve 2, $C = 1.130 + 4.18 \times 10^{-4} \times T(°C)$ kJ kg^{-1} K^{-1}; curve 3, $C = 1.243 + 4.60 \times 10^{-4} \times T(°C)$ kJ kg^{-1} K^{-1}.

(iii) Heat capacity plays an important role in the heat flux–time history at the composite–mould interface. At the beginning of the process and over the heating stage, a lower heat capacity is associated with a lower heat flux at the interface, the negative value indicating that the composite is being heated. During the cure stage, the same result is observed, and the lower the heat capacity the higher the maximum of the heat flux. Moreover, with a lower capacity, this maximum heat flux is attained in a shorter time.

CONCLUSIONS

The effect of the thermal parameters of the composite on the curing of this composite in a mould is of great importance. The heat capacity and thermal conductivity were examined by varing the value of each parameter in succession and by applying a previously tested numerical model.

Overall, the heat capacity is the most important factor because it influences both the heat conduction and the heat generated by the cure reaction. The lower the heat capacity, the shorter the heating period and the higher the increase in temperature in the resin due to the exothermic reaction.

The thermal conductivity influences only the heat conduction. The higher the thermal conductivity, the shorter the heating period and the lower the temperature maximum within the resin.

In general, the thermal conductivity of the final solid is different from that of the initial resin. A good knowledge on the effect of these parameters on the cure process is of both theoretical and practical importance, and thus provides information relevant to the synthesis of composites.

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