

Deconvolution of the thermal effects of the heat of conduction and heat of cure reaction for an unsaturated polyester

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(Received 8 September 1993; accepted 20 January 1994)

Abstract

Bulk moulding compound (BMC) composites have been cured in heated moulds, following an irreversible reaction which transforms the polymer into a three-dimensional network. The process is very complex because conduction heat transfer is associated with the heat evolved from the cure reaction. Modelling of this process is necessary, enabling simulation of the process and thus providing more information than experiments. The deconvolution of the two phenomena, heat transfer and chemical reaction, allows one to understand better the evolution of the process and to optimize the operational conditions. The contributions to the rise in temperature from heat conduction and chemical reaction have different histories in different parts of the composite, and can explain the temperature-, state-of-cure-, or heat-flux-time histories. The reaction-rate-time history is very sensitive in the earlier stages of curing, and supplements information obtained from the state-of-cure histories. The study was made on a thin sheet of composite in a metallic mould heated by oil, with one-dimensional heat transfer. The analysis was made using a numerical method that has been previously described and tested.

LIST OF SYMBOLS

C_n	specific heat capacity for the composite at position n
C_m	constant specific heat capacity for the mould
E	activation energy
k_0	pre-exponential factor
p	order of the overall reaction
R	universal gas constant
$MR_n, M_m,$ A, B, N	dimensionless numbers defined in eqns. (4), (6), (8) and (10), respectively
D, F	numbers defined in eqn. (8)

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n	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
S_i	function defined in eqn. (11)
SOC	state of cure
HF	heat flux
T_n, TN_n	temperature at position n , at times t and $t + \Delta t$, respectively
T_{oil}	temperature of heating oil
Δt	finite time increment
$\Delta x_m, \Delta x_r$	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
$(DTT)_n, (DTR)_n$	increase in temperature due to heat transfer and to the heat of cure respectively, at position n over the interval of time $[i\Delta t, (i + 1)\Delta t]$
$(DCR)_n$	specific reaction heat flow at the position n and time $i\Delta t$

INTRODUCTION

Bulk moulding compounds (BMC) are cured in a heated mould at a temperature sufficiently high for the cure reaction to start. At this temperature, the polymerization process transforms the highly viscous composite into a solid three-dimensional network [1].

Various factors add to the complexity of the process.

(i) The chemical reactions involved in the cure (co-polymerization of unsaturated polyester with styrene and other secondary reactions) are very complex and it is difficult to obtain an actual phenomenological model.

(ii) A numerical model is of practical use, the parameters of which can be determined by differential scanning calorimetry (DSC) [1].

(iii) The high sensitivity of the cure reaction to temperature creates the conditions for auto-acceleration.

(iv) A complex mechanism of heat transfer, involving conduction through the mould and composite, and convection at the mould–oil interface, coupled with the highly exothermic reactions makes an experimental investigation difficult.

(v) The relatively low thermal conductivity of the composite hinders elimination of the reaction heat, allowing a high increase in temperature and the development of steep temperature gradients within the composite.

(vi) Industrial operations have to be realized in optimal conditions [2–4].

A good knowledge of the process and proper control of these difficulties can be made possible by combining modelling and experiments [1], as a numerical model allows a quantitative evaluation of the process. In earlier papers, analysis was made using the temperature–time and state-of-cure–time histories in the middle of a long cylinder or at the mid-plane of a thin sheet [5–8], or using the heat-flux–time history and heat-flux profiles developed through a thin sheet [9, 10]. In this respect, the influence of various operational conditions [8], and of the thermal [10, 11] or kinetic [12, 13] parameters may be stated. It has also been possible to develop various techniques for optimizing the best industrial operations [8, 14].

The purpose of this paper is to show new possibilities for investigating the cure of BMC composites by deconvolution, distinguishing between the effects of conduction heat transfer and curing heat. To this end, the shapes of the different temperature–time, state of cure (SOC)–time and heat-flux–time histories at various sites in a plane sheet are determined and studied. The BMC composite is cured in a metallic mould, heated by stirred oil kept at a constant temperature. The slightly modified numerical model enables one to obtain histories of the contributions of heat transfer and of chemical reaction to the rise in temperature at different places in the sheet. The reaction-rate–time histories are compared with the SOC–time and heat-flux–time histories, providing a good explanation of their shape.

THEORETICAL

Assumptions

In order to build up the model for the cure process in a composite sheet, the following assumptions are made.

(i) One-dimensional heat transfer is considered. This is valid for a thin sheet, where edge effects are negligible.

(ii) Heat is transferred by conduction within the composite and mould, and by forced convection at the mould–oil interface.

(iii) The rate of heat generation from the exothermic cure reaction is expressed by p -order kinetics with respect to the ratio of the heat not yet evolved at time t and the total heat of reaction. The rate constant is temperature dependent following an Arrhenius equation. The kinetic and thermal parameters are assumed to be constant, except for the specific heat and thermal conductivity.

(iv) At the mould–composite interface, the thermal contact is assumed to be perfect, so that no thermal resistance is introduced by this interface.

(v) The temperature of the heated oil is kept constant over the whole process, but different from that of the mould.

(vi) The dimensions of the mould and composite are constant during the process.

Mathematical treatment

The basic equation for a uni-directional heat conduction in an isotropic solid, with internal heat generated by the cure reaction, is [1]

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

The right-hand side indicates the contributions from heat conduction and heat of reaction to the process. The rate of heat evolution by the exothermic chemical reaction is expressed by the classical equation [1]

$$\frac{\partial}{\partial t} \left(\frac{Q}{Q_\infty} \right) = k_0 \left(1 - \frac{Q}{Q_\infty} \right)^p \exp \left(- \frac{E}{RT} \right) \quad (2)$$

Numerical analysis

The cure reaction term in eqn. (1) which also depends on temperature, does not allow one to obtain an analytical solution. In order to resolve the problem, an explicit numerical method with finite differences is used.

The principle of the method, shown in earlier studies [1–6], consists of dividing the composite and the mould into intervals of constant thicknesses ($2N_r$ intervals of Δx_r width in the composite and N_m intervals of Δx_m width in each mould slab). Each limit of these intervals is a grid-point associated with an integer. The heat balance during the incremental time Δt in each slice surrounding a grid-point is evaluated by considering the heat conduction through the mould and resin, and the heat evolved from the cure reaction in the composite.

Temperature profiles

The new temperature after a time interval Δt is expressed in terms of the previous temperature at the same and adjacent places.

Within the composite $0 \leq n < N_r$,

$$TN_r = \frac{1}{MR_n} [T_{n+1} + (MR_n - 2)T_n + T_{n-1}] + \frac{\Delta Q_n}{C_n} \quad (3)$$

where MR_n is a dimensionless number

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

and ΔQ_n is the amount of heat generated by the cure reaction per unit mass, during the increment of time Δt at position n .

Within the mould $(N_r + 1) \leq n \leq (N_T - 1)$

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

where M_m is a constant dimensionless number

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

Composite–mould interface, with $n = N_r$

Half-slices in the composite of thickness $\Delta x_r/2$ and in the mould of thickness $\Delta x_m/2$ are considered. Using the same method, the new temperature TN_{N_r} is thus given by

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

where the coefficients A , B , D are expressed

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

$$F = \left(\rho C \frac{\Delta x}{2} \right)_r + \left(\rho C \frac{\Delta x}{2} \right)_m$$

Mould–oil interface, with $n = N_T$

A half-slice of thickness $\Delta x_m/2$ is considered. The new temperature of the external mould surface TN_{N_T} is given by

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

where T_{oil} is the constant oil temperature, sufficiently different from the mould surface. The dimensionless number N is expressed as a local Nusselt number

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

h being the heat transfer coefficient at the oil–mould interface.

State of cure in the composite

In order to calculate the heat evolved by the exothermic cure reaction up to time $i\Delta t$ and hence the state of cure, the following integral function is considered

$$S_i = k_0 \int_0^{i\Delta t} \exp\left(-\frac{E}{RT_\theta}\right) d\theta \quad (11)$$

For a small time increment Δt , eqn. (11) can be approximated as

$$S_{i+1} = S_i + k_0 \Delta t \exp\left(-\frac{E}{RT_{i\Delta t}}\right) \quad (12)$$

with

$$S_0 = 0 \quad (13)$$

Integration of eqn. (2) gives

$$\frac{Q_\infty - Q_i}{Q_\infty} = [1 + (\rho - 1)S_i]^{1/1-p} \quad p \neq 1 \quad (14)$$

At each position n and time $i\Delta t$, at the state of cure is expressed as

$$\text{SOC}_{n,i} = 100 \frac{Q_{n,i}}{Q_\infty} \quad (15)$$

Conditions of stability

In order to maintain the stability of the calculations, the coefficients of the temperature T_n in the different equations (3), (5), (7) and (9) have to be positive, leading to

$$MR_n > 2 \quad M_m > 2N + 2 \quad 1 - A - B > 0 \quad (16)$$

Heat flux profile

As shown in an earlier paper [9], it is interesting to analyse the heat flux in various places.

Within the composite $0 \leq n < N_r$ and *within the mould*

$$(N_r + 1) \leq n \leq (N_T - 1)$$

The heat flux by conduction is calculated by a linear approximation with a second-order error

$$\text{HF}_n = -\lambda \left(\frac{\partial T}{\partial x}\right)_n = -\lambda \frac{T_{n+1} - T_{n-1}}{2\Delta x} \quad (17)$$

At the composite–mould interface, $n = N_r$

A parabolic approximation for the temperature profile is considered, and the heat flux becomes

$$\text{HF}_{N_r} = -\lambda_r \frac{3T_{N_r} - 4T_{N_r-1} + T_{N_r-2}}{2\Delta x_r} \quad (18)$$

At the mould–oil interface, $n = N_T$

A Newton-type formulation for the heat transfer flux is considered

$$HF_{N_T} = h(T_{N_T} - T_{oil}) \quad (19)$$

the heat flux being positive when heat leaves the mould and enters the oil.

Separation of the effects

From the relationships (3), (5), (7) and (9), it is possible to distinguish the effect of heat transfer by both conduction and heat of cure, on the change in temperature during each incremental time Δt . Additional relationships demonstrate the origin of each contribution.

Within the composite $0 \leq n < N_r$

Expression (3) becomes

$$TN_n = T_n + (DTT)_n + (DTR)_n \quad (20)$$

where

$$(DTT)_n = \frac{T_{n+1} - 2T_n + T_{n-1}}{MR_n} = \frac{(HF_{n-0.5} - HF_{n+0.5})\Delta t}{(\rho C_n)_r \Delta x_r} \quad (21)$$

is the increase in temperature due to conduction heat transfer and

$$(DTR)_n = \frac{\Delta Q_n}{C_n} = \frac{Q_\infty (\text{SOC}_{n,i+1} - \text{SOC}_{n,i})}{C_n} \quad (22)$$

is the increase in temperature due to the heat of cure over the interval of time $[i\Delta t, (i+1)\Delta t]$.

Composite–mould interface, $n = N_r$

The contribution of the heat conduction can be expressed as

$$(DTT)_{N_r} = AT_{N_r+1} - (A+B)T_{N_r} + BT_{N_r-1} = (HF_{N_r-0.5} - HF_{N_r+0.5}) \frac{\Delta t}{F} \quad (23)$$

In this case the contribution of the exothermal cure reaction is limited to the composite half-slice, being thus always smaller than in other sites in the composite

$$(DTR)_{N_r} = \frac{3\Delta Q_{N_r} + \Delta Q_{N_r-1}}{4} D \quad (24)$$

where A , B , D and F are given in eqn. (8), with $D < 1$.

Within the mould $(N_r + 1) \leq n \leq (N_T - 1)$

The heat conduction contribution has a similar form as in the composite (eqns. (20), (21))

$$TN_n = T_n + (\text{DTT})_n \quad (25)$$

$$(\text{DTT})_n = \frac{T_{n+1} - 2T_n + T_{n-1}}{M_m} = \frac{(\text{HF}_{n-0.5} - \text{HF}_{n+0.5})\Delta t}{(\rho C)_m \Delta x_m} \quad (26)$$

At the mould–oil interface, with $n = N_T$

The heat conduction contribution has the form

$$(\text{DTT})_{N_T} = \frac{1}{M_m} [2T_{N_T-1} - (2 + 2N)T_{N_T} + 2NT_{\text{oil}}] - \frac{(\text{HF}_{N_T-0.5} - \text{HF}_{N_T})\Delta t}{\left(\frac{\Delta x}{2} \rho C\right)_m} \quad (27)$$

where N is expressed in eqn. (10)

The specific reaction flow at each site in the composite is

$$(\text{DCR})_{n,i} = \frac{(Q_{n,i+1} - Q_{n,i-1})}{2\Delta t} \quad (28)$$

with

$$(\text{DCR})_{n,0} = \frac{(Q_{n,1} - Q_{n,0})}{2\Delta t} \quad (29)$$

EXPERIMENTAL

Materials

The BMC composite (Menzolite, France) used had the composition: maleic polyester resin, 16.0%; polyvinyl acetate, 10.7%; styrene, 4.1%; catalyst, 0.5%; hydrated alumina, 66.7%; magnesia, 0.1%; zinc stearate, 1.9%. 100 parts by weight of this mixture were mixed with 20 parts by weight of fibre glass.

Kinetic and thermal parameters

The values are given in Table 1. The kinetic parameters were calculated using the heat-flux–temperature curves obtained by differential scanning calorimetry (DSC 111, Setaram, France) at low heating rates ($0.5^\circ\text{C min}^{-1}$) using rather large samples (> 150 mg) because of the sample heterogeneity [15–19]. The heat transfer coefficient by forced convection is determined by superimposing experimental and calculated curves for the temperature–time

TABLE 1
Kinetic and thermal parameters

Composite	Duralumin mould
$k_0 = 11 \times 10^{21} \text{ s}^{-1}$	$\rho = 2.700 \text{ kg m}^{-3}$
$E = 181.2 \text{ kJ mol}^{-1}$	$C = 0.92 \text{ kJ}^{-1} \text{ K}^{-1}$
$P = 2.30$	$\lambda = 123.7 \text{ J s}^{-1} \text{ m}^{-1} \text{ K}^{-1}$
$Q_\infty = 75.2 \text{ kJ kg}^{-1}$	Coefficient of heat transfer by forced convection
$\rho = 1.770 \text{ kg m}^{-3}$	$h = 334 \text{ J m}^{-2} \text{ s}^{-1} \text{ K}^{-1}$
$C = 1.13 + 4.18 \times 10^{-4} T / ^\circ\text{C} \text{ kJ kg}^{-1} \text{ K}^{-1}$	
$\lambda = 1.00 \text{ J s}^{-1} \text{ m}^{-1} \text{ K}^{-1}$ for $\text{SOC} < \text{SOC}_{\text{MAX}}$	
$\lambda = 1.38 \text{ J s}^{-1} \text{ m}^{-1} \text{ K}^{-1}$ for $\text{SOC} > \text{SOC}_{\text{MAX}}$	

histories in the centre of a composite that had been cured, under the same conditions as those selected for the cure of the resin. The specific heat varies linearly with temperature. The thermal conductivity is assumed to change at a given value of the state of cure.

Moulding and heating system

A thin thermocouple of K types was embedded in the middle of a 7.0-mm thick, 34-mm diameter sheet of composite. The composite was pressed by the slabs of the mould, 57 mm in diameter and 3.8 mm in thickness. The system, previously at room temperature, was immersed in a silicone oil bath ($146 \pm 0.5^\circ\text{C}$ and a controlled stirring speed of 500 rpm). The temperature in the middle of the composite was recorded [6].

RESULTS

Because the process is highly complex for thermosets, involving heat transfer and internal heat generated by the cure reaction, it is necessary to have good information for the various stages of the process. Experiments are of help in providing the temperature–time histories at various places in the composite, especially along the mid-plane where better accuracy is obtained [5–7]. However, exhaustive investigation is possible only by using numerical models and calculations [8, 9]. Three kinds of information are considered in particular.

(i) The rate of heat generated by the cure reaction at various places within the thickness of the sample, as well as the rate of cure, both these pieces of information being expressed as a function of time.

(ii) The temperature–time histories at various places throughout the thickness of the sample, as well the contribution to the heat change due to heat transfer and reaction heat.

(iii) The heat-flux–time histories at various places throughout the composite.

Cure reaction within the sample

The cure reaction developed within the sample is studied by considering either the rate of heat generated by the reaction as a function of time or the state-of-cure–time history. Three places within the sample are selected: the

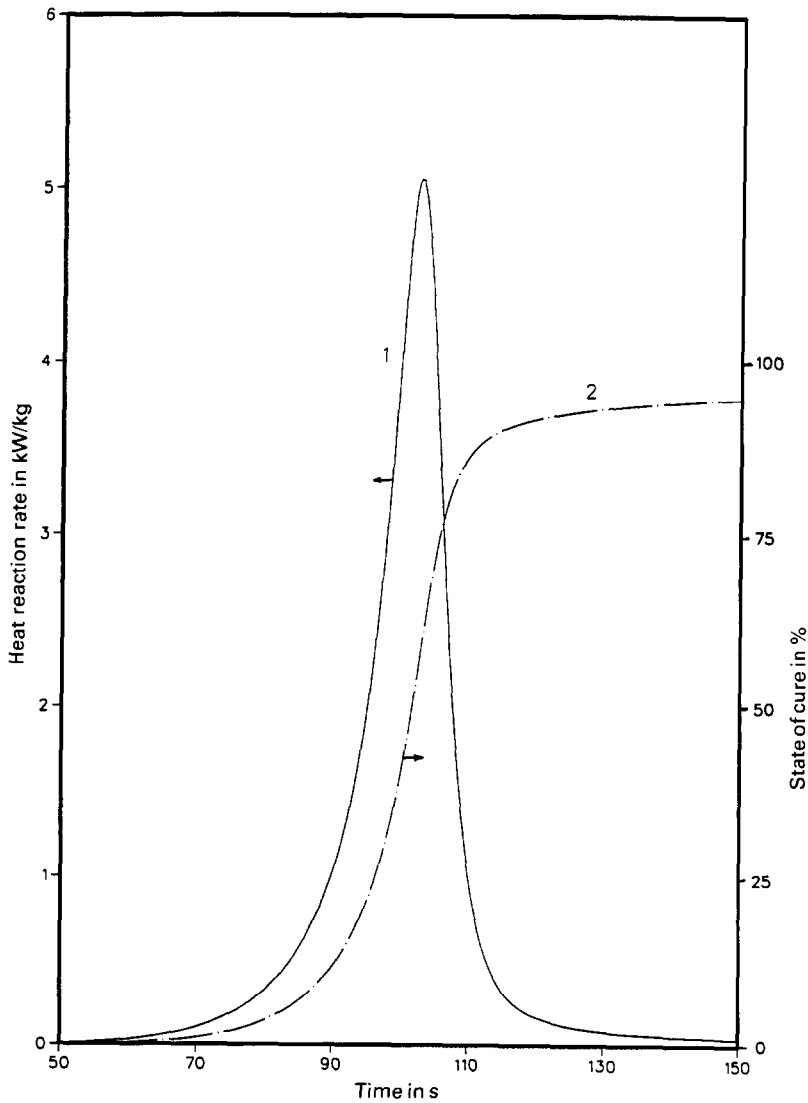


Fig. 1. Rate of heat evolved from the cure reaction (1) and state of cure (2) as a function of time, at the mid-plane of the composite.

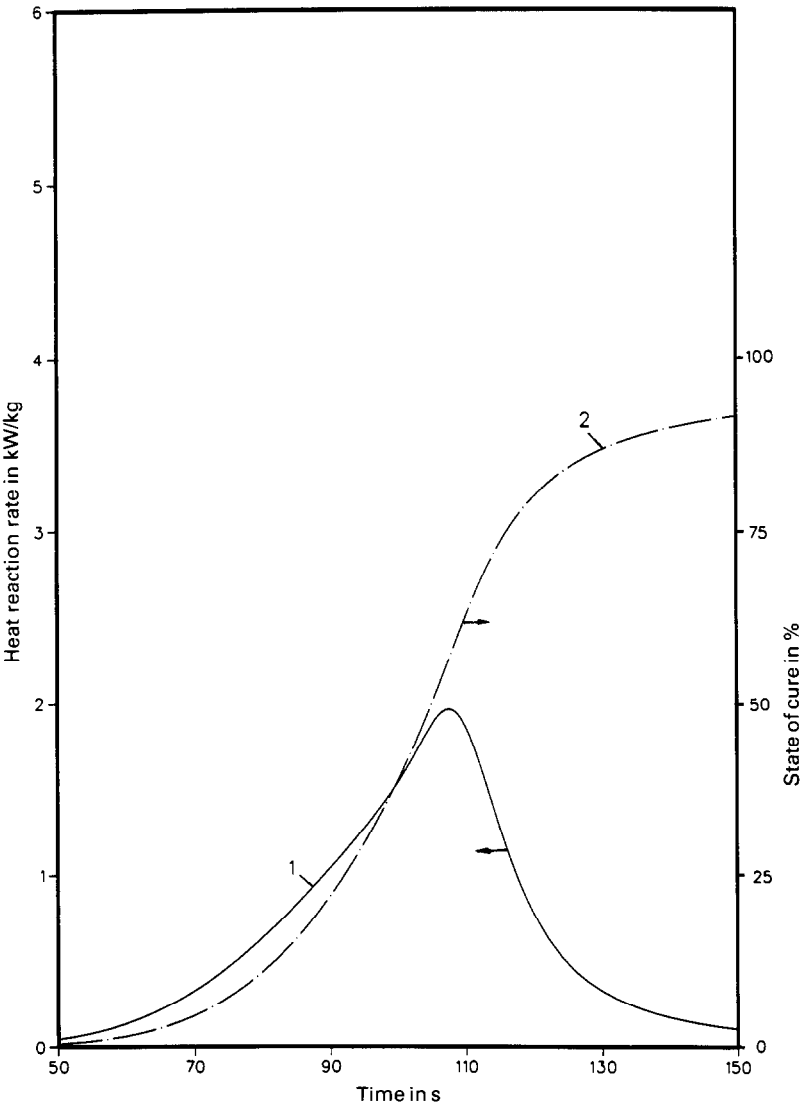


Fig. 2. Rate of heat evolved from the cure reaction (1) and state of cure (2) as a function of time, at the composite–mould interface.

mid-plane of the sample (Fig. 1), or the surface of the sample in contact with the mould (Fig. 2), and the plane parallel to the composite–mould interface located between the middle of the mid-plane and the interface (Fig. 3).

The curves drawn in each of these three figures are of interest, and comparison between the shapes of these curves lead to the following conclusions.

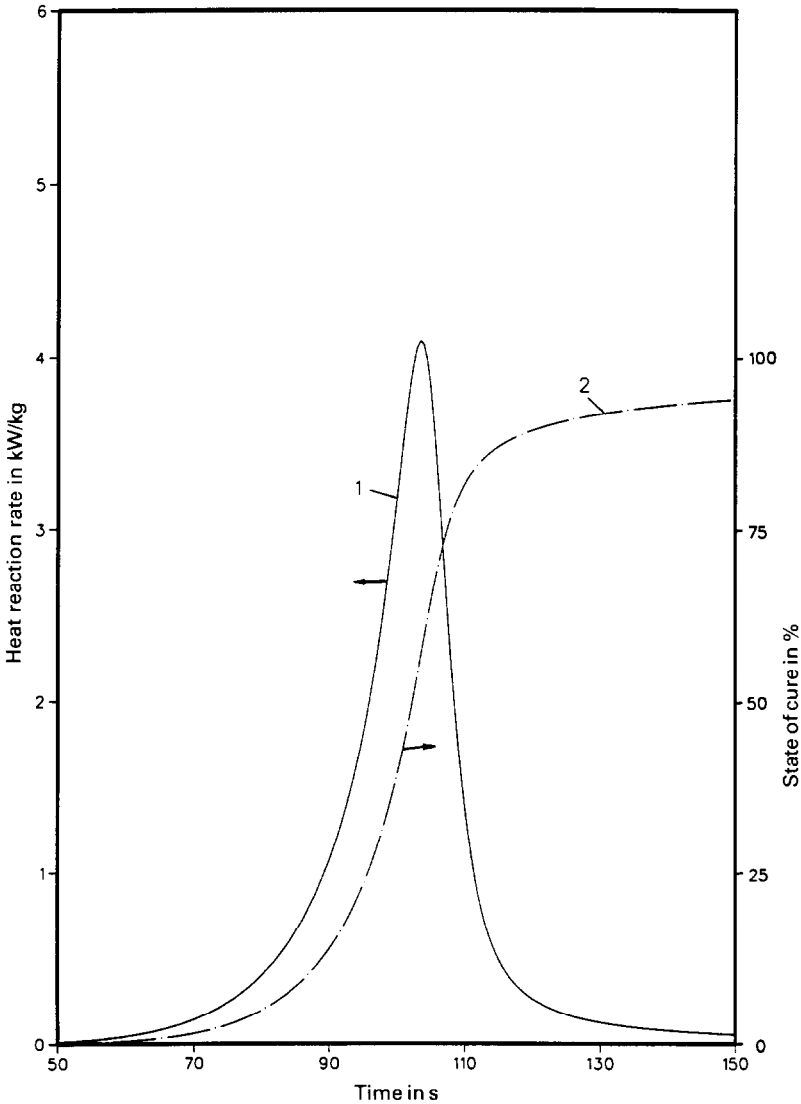


Fig. 3. Rate of heat evolved from the cure reaction (1) and state of cure (2) as a function of time in the plane located between the midplane and the composite surface.

(i) The rate of heat evolved from the cure reaction in various places within the sample varies with time, following a typical pattern: the rate increases up to a maximum and then decreases down to zero.

(ii) The state of cure increases continuously up to a high value. The rate of increase in the state of cure is given by the rate of heat evolved from the cure reaction.

(iii) The shape of these two curves shown in (i) and (ii) varies considerably with position in the sample.

(iv) The rate–time history for the heat evolved from the reaction reaches a higher value at the mid-plane of the composite and a lower value at the composite–mould interface.

(v) The shape of the curves in (iv) depends on the position within the sample, i.e., sharp at the mid-plane, less so at the interface.

(vi) The time at which the reaction starts may also be of interest. The reaction starts on the surface of the composite, and progresses towards the mid-plane of the sample.

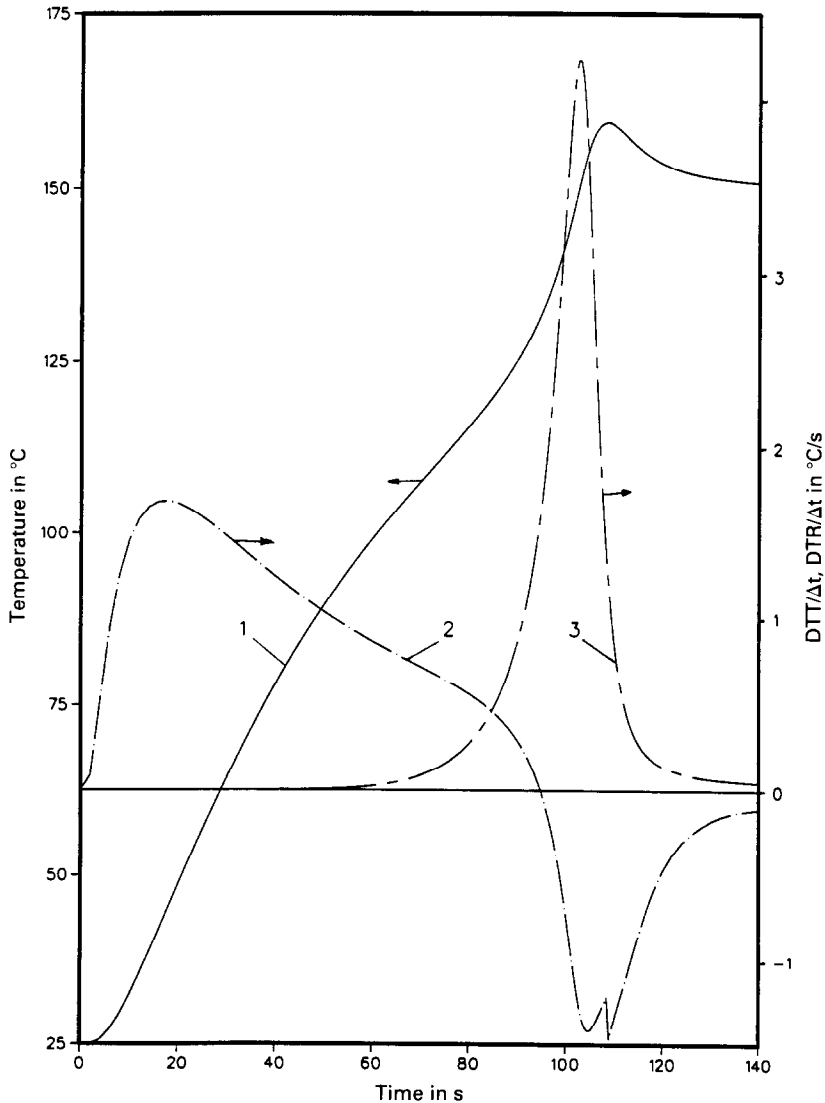


Fig. 4. Temperature–time history (1), and contribution due to conduction heat transfer (2) and internal heat generated by the cure reaction (3), at the mid-plane of the composite.

Temperature–time histories at various places

Temperature–time histories are complementary to the state-of-cure–time histories. These temperature–time histories are drawn (curve 1) for various places within the composite: at the mid-plane in Fig. 4, on the surface of the resin in Fig. 5, and at the plane located between the mid-plane and the interface, in Fig. 6.

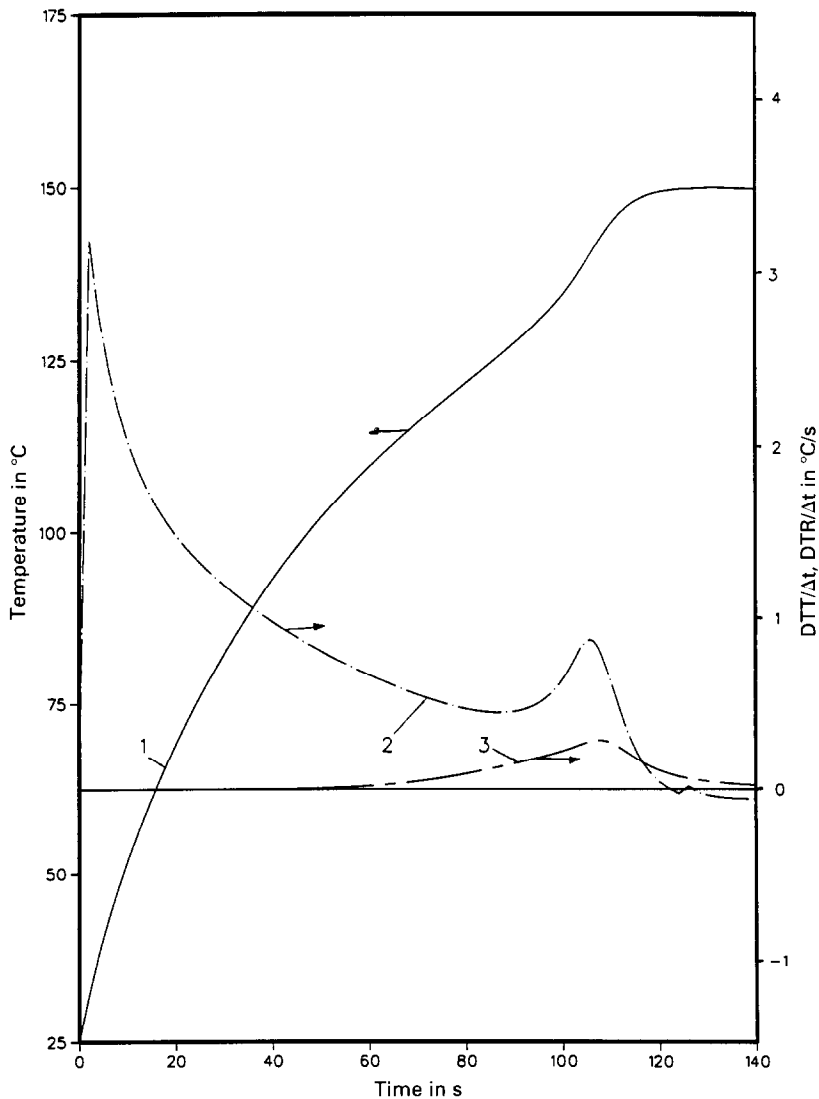


Fig. 5. Temperature–time history (1), and contribution due to conduction heat transfer (2) and internal heat generated by the cure reaction (3), at the composite–mould interface.

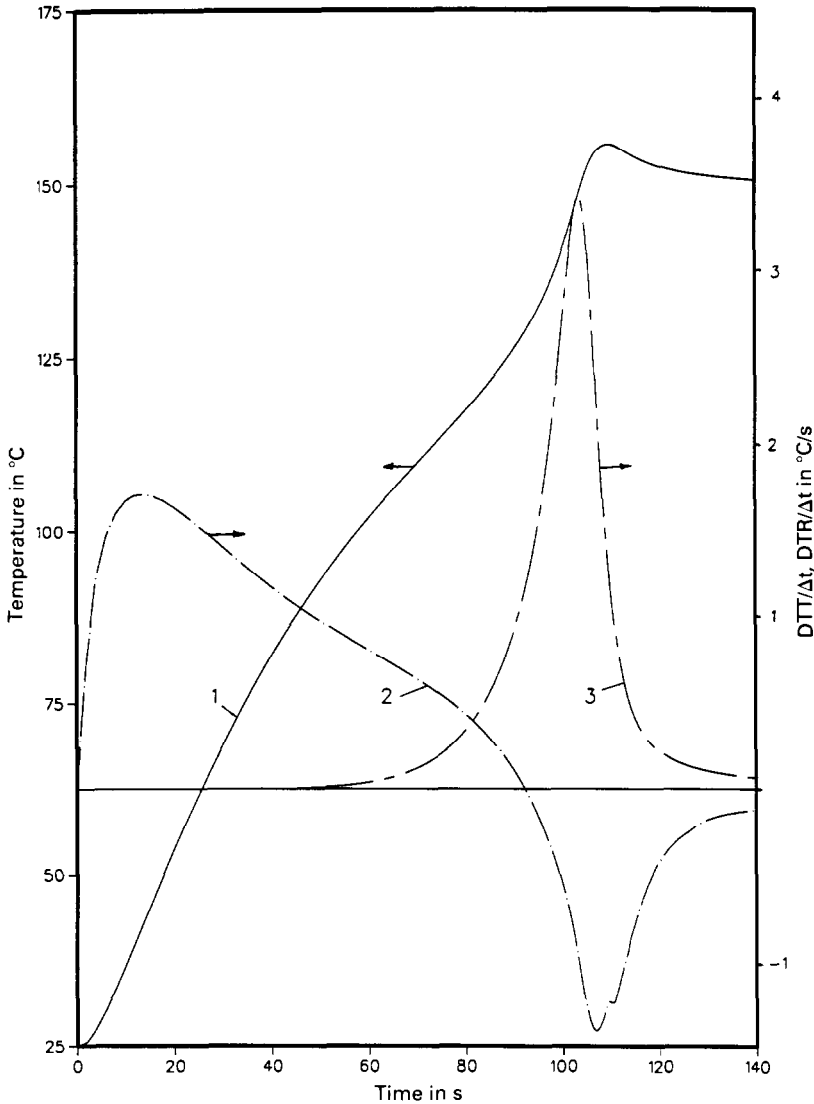


Fig. 6. Temperature–time history (1), and contribution due to conduction heat transfer (2) and internal heat generated by the cure reaction (3), in the plane between the mid-plane and the composite surface.

In addition, the contribution of the change in temperature resulting from the conduction heat transfer (curve 2) and from the heat generated by the cure reaction (curve 3) are plotted.

Comparisons made between these curves in Figs. 4–6 leads to the following interesting conclusions.

(i) The temperature–time histories vary slightly with position. These curves pass through a maximum which is very clear within the composite and very slight on its surface, maximum being higher at the mid-plane.

(ii) It takes some time for heat to be transferred by conduction through the composite, resulting in a time delay for the increase in temperature within the composite, this delay being greater at the mid-plane.

(iii) The contribution of the conduction heat transfer to the increase in temperature is apparent in curves 2 of each figure. It is very high at the beginning of the process on the surface of the composite.

(iv) The contribution of the internal heat generated by the cure reaction is more simple to understand. These curves (curve 3 in each figure) are

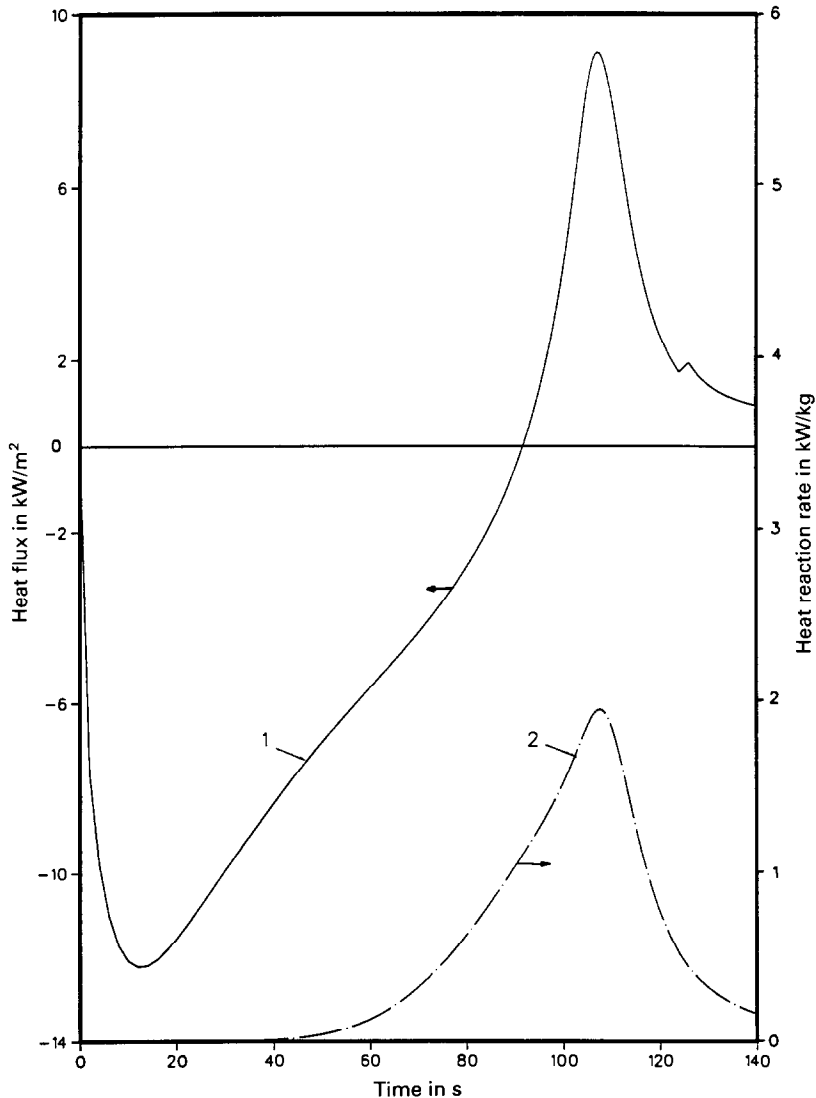


Fig. 7. Heat-flux-time history (1) and rate of heat evolved from the cure reaction (2) at the composite-mould interface.

nearly homothetic with the curves expressing the rate of reaction heat shown in Figs. 1–3.

(v) The shapes of the curves expressing the contribution of the conduction heat transfer are significantly modified when the cure reaction starts, becoming negative. This is due to the fact that heat generated by the cure reaction is evacuated by conduction heat transfer.

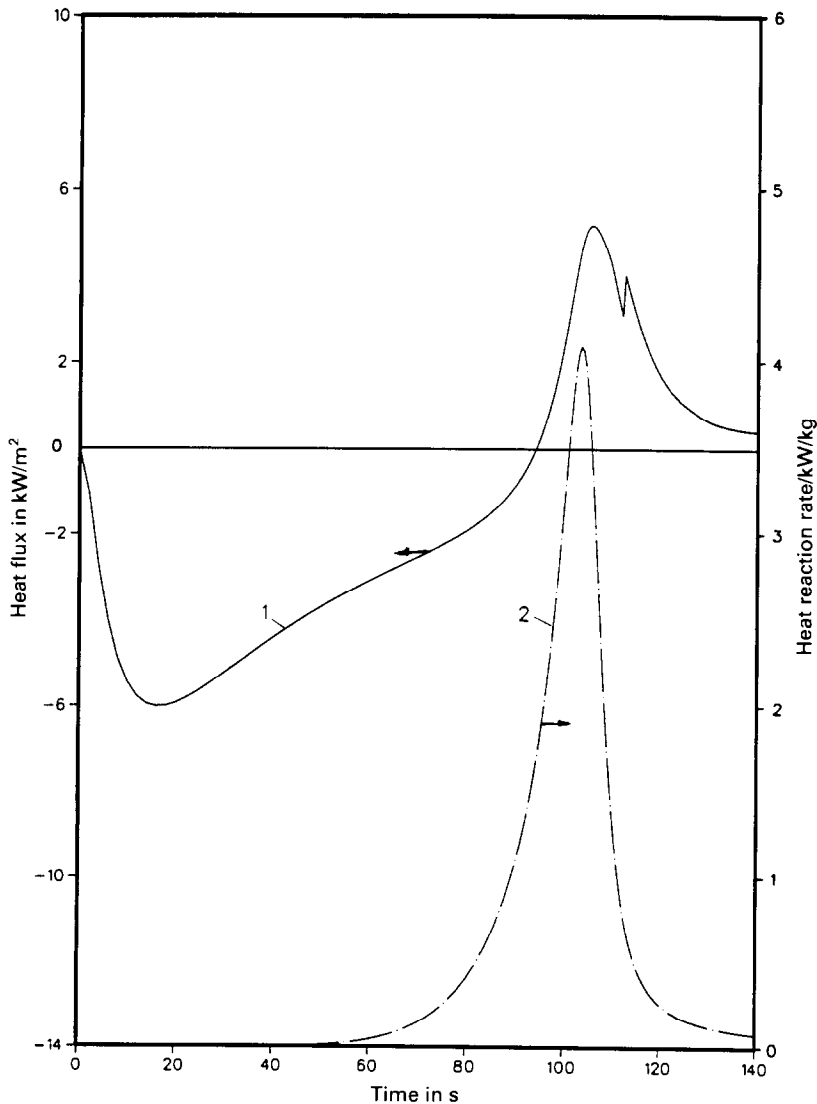


Fig. 8. Heat-flux–time history (1) and rate of heat evolved from the cure reaction (2) in the plane located between the mid-plane and the composite surface.

Heat-flux–time histories

As already indicated in a previous study [9], the heat-flux–time histories developed at various places within the composite are of great interest. These heat-flux–time histories (curve 1) are drawn in two places: at the surface of the composite in contact with the mould (Fig. 7), and in the plane located between this interface and the mid-plane of the composite (Fig. 8). Because the mid-plane is a plane of symmetry, the heat flux is constantly zero there. The rate of heat evolved from the cure reaction is also drawn in Figs. 7 and 8 (curve 2). The heat-flux–time histories developed within the sample are important pieces of information, from both a theoretical and a practical point of view.

(i) The shape of the heat-flux–time histories varies with position. Completely flat at the mid-plane of the sample, greater amplitude is exhibited at the composite–mould interface.

(ii) The heat-flux–time history displays a rather complex pattern, depending on the effect of conduction heat transfer and heat evolved from the cure reaction.

(iii) The heat flux is firstly endothermic, i.e. heat is transferred from the mould to the inside of the composite, and then becomes exothermic, i.e. heat is transferred within the composite towards the mould.

(iv) The heat-flux–time history at the composite–mould interface is very useful from a practical point of view. It can easily be measured with a heat-flux meter on the surface of the mould. Moreover, this measurement does not destroy the sample.

CONCLUSIONS

This method of combining experiments and modelling is attractive in research, as it enables one to obtain a fuller insight into the nature of the process. Moreover, when the process is complex, analysis of the pieces of information obtained by calculation is fruitful.

By considering the reaction–cure–time temperature–time and heat-flux–time histories developed within the sample, a more extensive knowledge of the process can be obtained. The effect of the conduction heat transfer through the composite and of the internal heat generated by the cure reaction is clearly shown, despite the complexity of the process.

Finally, from an essentially practical point of view, the heat-flux–time history at various places, especially at the composite–mould interface, provides an improved way of following the reaction and also of controlling the process using various means [5, 7, 14].

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