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MODELLING OF PROCESSES IN CALORIMETRY BY TAKING INTO ACCOUNT HEAT TRANSFER AND REACTION *

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ABSTRACT

The processes developed in the sample in calorimetric techniques are modelled by considering the reaction and heat transfer by conduction. The reaction studied is the cure of an epoxy resin of high enthalpy (~ 76 cal g^{-1}). Heat is transferred through the sample and the mould–sample interface by conduction. The model, based on an explicit numerical analysis, can give information on the heat flux–time history and the profiles of temperature and state of cure developed through the sample. The two main calorimetric techniques are considered: differential scanning calorimetry and isothermal calorimetry. Various factors are considered, such as the temperature in differential calorimetry, the heating rate in the scanning mode and a change in the enthalpy of cure.

INTRODUCTION

In both differential scanning calorimetry (DSC) and differential calorimetry (DC), the enthalpy changes accompanying a chemical or physical event in the sample are monitored. The result is a profile of the rate of enthalpy change either as a function of temperature, as the sample is heated at a known linear rate (DSC), or as a function of time, the calorimeter being held at constant temperature (DC). Detailed kinetic analysis of these enthalpy profiles is only possible in the case of simple reactions. Although the determination of meaningful kinetic parameters for complex reactions is not feasible, it is very often of interest to obtain the kinetic parameters of the overall reaction [1–4].

In the DC experiment, the enthalpy of reactions occurring at the constant applied temperature is determined up to some given time. The applied temperature is the set calorimeter temperature and not the true sample

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* Dedicated to Professor W.W. Wendlandt on the occasion of his 60th birthday.

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temperature during the reaction, not only because of local heating arising from the exothermic reactions [1] but also because of heat transferred by conduction or convection through the oven–holder interface [5–7]. Moreover, as a result of heat transferred by conduction through the material and exothermic reactions, some gradients of temperature are developed through the material itself. These above facts are, of course, responsible for the development of other gradients of the rate of reaction through the sample [5–8].

In the DSC experiment, the fresh sample is scanned at a selected heating rate up to a temperature at which the reaction exotherm is complete. Heat is transferred under transient conditions during the whole process by convection through the oven–holder interface and by conduction through the material. The rate of heat transfer is generally low, especially when compared with the rate of reaction, and this is responsible for two factors: (i) large gradients of temperature are established when no reaction occurs as shown previously [9]; (ii) other gradients of temperature are developed when the reaction takes place [6,7]. The heating rate has a significant effect on both these profiles, while the second type of profile is affected by the value of the reaction enthalpy.

The small sample size sometimes used in calorimetry necessitates that all ingredients in the sample are very well dispersed in the case of several components in the holder, and dispersion problems occasionally arise, usually seen in a lack of reproducibility in the enthalpy–time curve. Thus a better answer to the question of a representative sample is to use a calorimeter running with a rather large sample; but of course large samples necessitate the use of slower heating rates.

The main purpose of this paper is to compare the profiles of temperature and the profiles of the extent of reaction as they are developed through the sample either in DSC or DC, when the enthalpy of the reaction is rather high. Experiments done in these cases give the heat flux–time in DC and heat flux–temperature history in DSC. Modelling of the process can also determine the profiles of temperature and extent of reaction developed through the sample, as they are obtained as a function of time or temperature. Some previously described models [5–8], which take into account the heat transfer through the material and the oven–holder interface as well as the heat evolved from the overall reaction, are successfully used for this problem.

The cure of an epoxy resin is studied because of the high value of the cure enthalpy (~ 76 cal g^{-1}). Another aim of the paper is to determine the effect of a 5 cal g^{-1} change around the mean value of 76 cal g^{-1} on the cure process. These changes in enthalpy have been observed when the composition of the two components in a mixture is not controlled exactly [10]. For this reason, three values (71, 76, 81 cal g^{-1}) are considered for the enthalpy of the cure reaction.

THEORETICAL

Assumptions

The usual assumptions are made on the process.

(i) Only radical heat conduction was considered through the circular cross-section of the sample, the length of the cylinder being sufficiently long compared with the radius.

(ii) Thermal properties used in the study, such as thermal conductivity and heat diffusivity, are taken to be constant.

(iii) The temperature of the calorimeter oven is equal to the temperature of the surface of the material, the holder being made of a thin steel envelope.

(iv) The state of cure (SOC) of the resin at time t is expressed as the enthalpy evolved from the reaction up to time t as a fraction of the total enthalpy evolved.

(v) The kinetics of the cure reaction of the resin are described by a simple reaction, with a constant order and activation energy. This equation was previously found to give results in good agreement with experiment [6,8,11] and its kinetic parameters are more simply determined than with other complicated equations [12,13].

Mathematical treatment

Following the above assumptions, the rate of temperature rise in the material is given by the equation of heat conduction when internal heat is generated by the exothermic reaction:

$$\rho C \frac{\partial T}{\partial t} = \lambda \frac{\partial^2 T}{\partial r^2} + \rho \frac{\mathrm{d}Q}{\mathrm{d}t} \tag{1}$$

In DC experiments, the temperature of the calorimeter is constant, and the sample previously at room temperature is heated to this constant temperature.

In DSC, the temperature of the calorimeter increases constantly from room temperature to the final temperature at which the full exotherm is obtained.

$$T_{i,R} = T_{i-1,R} + b\Delta t \tag{2}$$

The initial and boundary conditions are:

$$t = 0 \quad 0 \leqslant r \leqslant R \quad T \text{ sample} \tag{3}$$

$$t > 0 \quad r > R \quad T \text{ calorimeter}$$

$$0 < r < R \quad T \text{ sample} \tag{4}$$

The kinetics of heat evolved up to time t from the cure reaction are expressed by eqn. (5), following assumption (v):

$$\frac{1}{Q_\infty} \frac{\mathrm{d}Q_t}{\mathrm{d}t} = k_0 \left(1 - \frac{Q_t}{Q_\infty}\right)^n \exp - \frac{E}{RT} \tag{5}$$

No analytical solution can be found for eqn. (1), because of the presence of internal heat from the cure reaction expressed by eqn. (5). The problem is solved by using a numerical method with finite differences.

The circular cross-section of the sample is divided into circles of radii r, $r+\Delta r$, $r+2\Delta r$, and the radius of the sample is given in Fig. 1.

The heat balance determined in the ring located between the radii $r+\Delta r/2$ and $r-\Delta r/2$ enables us to obtain the temperature in the ring at the time $(i+1)\Delta t$ as a function of the temperatures obtained at the preceding time in the same ring and in the two adjacent rings.

$$T_{i+1,r} = \frac{1}{M_{i,r}}\left[T_{i,r+\Delta r} + (M_{i,r}-2)T_{i,r} + T_{i,r-\Delta r}\right] + \frac{\Delta r}{2Mr}\left[T_{i,r+\Delta r} - T_{i,r-\Delta r}\right] + \frac{1}{C}\frac{\mathrm{d}Q}{\mathrm{d}t}\Delta t \tag{6}$$

Equation (6) is not applicable to calculating the temperature at the middle of the cross-section ($r=0$), and the following equation is used in this case:

$$T_{i+1,0} = \frac{4}{M_{i,0}}\left[T_{i,\Delta r} - T_{i,0}\right] + \frac{1}{C}\frac{\mathrm{d}Q}{\mathrm{d}t}\Delta t \tag{7}$$

In both eqns. (6) and (7), the dimensionless number M is given as follows, in terms of the increments of space Δr and time Δt:

$$M = \frac{(\Delta r)^2}{\Delta t}\frac{\rho C}{\lambda} \tag{8}$$

The value of this model is that it allows the user to calculate the heat flux emitted through the calorimeter–holder interface. From assumption (iii), the

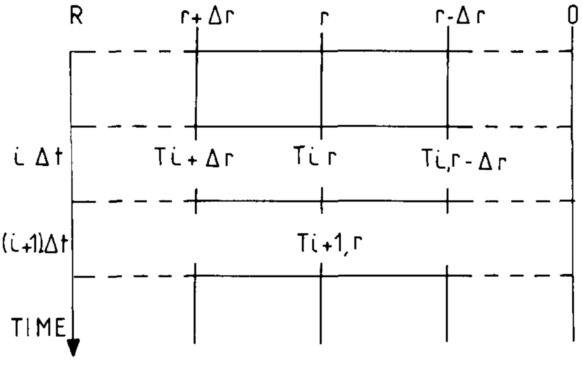

Fig. 1. Space–time diagram for numerical analysis.

heat flux (HF) is proportional to the gradient of temperature near the surface of the sample.

$$\mathrm{HF} = \lambda \frac{T_R - T_{R-\Delta r}}{\Delta r} \tag{9}$$

Another advantage of this model is the ease with which the extent of heating is evaluated as a function of time and space [6–8]. This is certainly an important advantage over other models which only deliver the temperature profile [14,15]. The heat evolved from the cure reaction is calculated with the following recurrent relation:

$$\left(\frac{\mathrm{d}Q}{\mathrm{d}t}\right)_{t+1} \Delta t = Q_{t+1} - Q_t = k_0 (Q_\infty - Q_t)^n Q^{1-n} \exp\left(-\frac{E}{RT}\right) \Delta T \tag{10}$$

with

$$Q_t = \sum_{i=0}^{i} \left(\frac{\mathrm{d}Q}{\mathrm{d}t}\right)_i \Delta t \text{ and } Q_0 = 0$$

The state of cure (SOC) is obtained by the ratio:

$$\mathrm{SOC}_t = \frac{Q_i}{Q_\infty} \times 100 \tag{11}$$

EXPERIMENTAL

The calorimeter used in this work (Setaram DSC 111) can work either under isothermal conditions or in the scanning mode.

About 100–200 mg of resin is encapsulated in the holder. This holder is a cylinder of 5 mm diameter.

The calorimeter is coupled with a microcomputer (MP 86) which can store the data in a first run, to determine the SOC value at any time in the second run and the kinetic parameters during the third run.

The formulation used in this study is based on mixtures of 2605 epoxy resin containing DGEBA epoxy molecules with an anhydride hardener and tertiary amine as catalyst. The formulation investigated contained 80 parts of hardener per 100 parts of resin, by weight.

TABLE 1

Values of parameters

Kinetic properties		
$n = 1.5$	$k_0 = 4 \times 10^{11}$ s^{-1}	$E = 27{,}140$ cal mol^{-1}
$\Delta H = 76$ cal g^{-1}	$\Delta H = 71$ cal g^{-1}	$\Delta H = 81$ cal g^{-1}
Thermal properties		
$\lambda = 1.85 \times 10^{-3}$ cal cm^{-1} s^{-1} K^{-1}		$C = 0.5$ cal g^{-1} K^{-1}

The values of the parameters characterizing the kinetics of reaction and heat transfer are shown in Table 1.

The value of the cure enthalpy obtained from DSC experiments is ~ 76 cal g^{-1}, but a change of 5 cal g^{-1} around this mean value is very often seen due to the difficulty of proper mixing of the two components [9].

RESULTS

The technique of modelling is applied successively to isothermal conditions (DC) and those with constant heating rates (DSC).

Calorimetry under isothermal conditions (DC)

Experiments can obtain the positive part of the heat flux–time history when this heat flux is emitted from the sample to the calorimeter detector.

Modelling affords a further insight into the nature of the process and the reaction, since it is able not only to describe the total history of the heat flux, but also to determine the profiles of temperature and SOC developed through the sample.

Heat flux–time history

It is easy to obtain the full heat flux–time history from the beginning to the end of the process using the model. As shown in Fig. 2, where the heat flux is expressed as a function of time, two steps can be differentiated when the temperature of the calorimeter is constant at 160 °C.

(i) The first stage appears when the heat flux is negative. This corresponds to the heating of the material and holder by the calorimeter oven. Of course, this heat flux is very high, especially at the time the holder is introduced into the calorimeter, when the difference between the temperatures of the calorimeter and holder is greatest.

(ii) The second stage can be realized when the heat flux is positive, the holder and sample being hotter than the calorimeter.

When the reaction exotherm is complete, it is useful to extract the holder and sample from the calorimeter, cool them to room temperature, and put the sample into the calorimeter again. This part of the experiment is necessary for obtaining the reference baseline more easily than by waiting a long time until the heat flux becomes constant. This reference baseline is obtained with the model when the constant reaction rate is zero.

An interesting point can be noted from the curves in Fig. 2: the area between the heat flux–time curves obtained with reaction ($k_0 \neq 0$) and without reaction ($k_0 = 0$) corresponds to the evolution of the cure reaction. As shown in this figure, this area is larger than the positive part of the heat flux–time curve generally determined experimentally, because the cure reac-

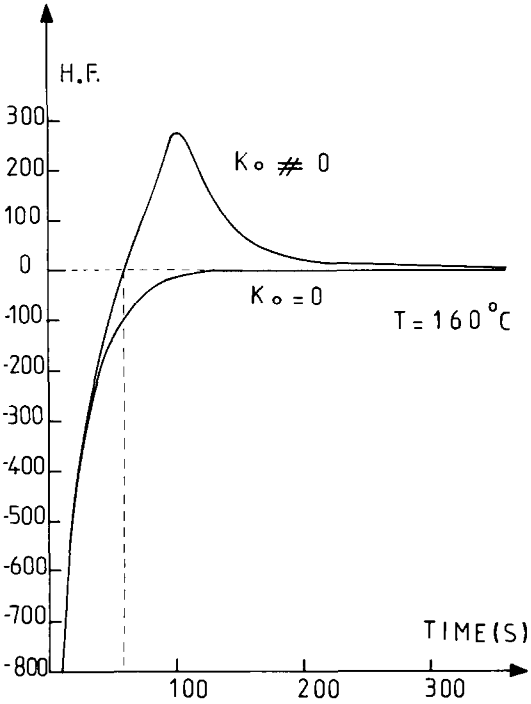

Fig. 2. Total heat flux–time history under isothermal conditions. $T = 160\,^\circ C$.

tion starts during heating of the sample when the heat flux is endothermic. This causes the lower values of enthalpy obtained by DC compared with those determined by DSC. Moreover, we can see that the first part of the exothermic reaction is not obtained with experimental measurements; this drawback of the technique may be major in some cases, when this part of the reaction corresponds with initiation reactions (cure of rubber, resins).

Two experimental limitations on the temperature range over which meaningful data can be obtained result from these observations: (1) the lowest temperature is determined by the sensitivity and stability of the calorimeter, the rate of enthalpy change being too small to the recorded when the cure rate is very low; (2) the highest temperature at which measurements can be obtained is determined by the induction time necessary for initiation. If the induction period is shorter than the time required for the calorimeter to establish thermal equilibrium after the sample is introduced, the first part of the exotherm is not obtained. In conclusion, a temperature range of 20–40 °C is found over which meaningful data can be obtained, the size of the range depending on the activation energy of the reaction.

It is of course difficult to appreciate the effect of the temperature chosen for the calorimeter on the change in the kinetics of the reaction. However, it

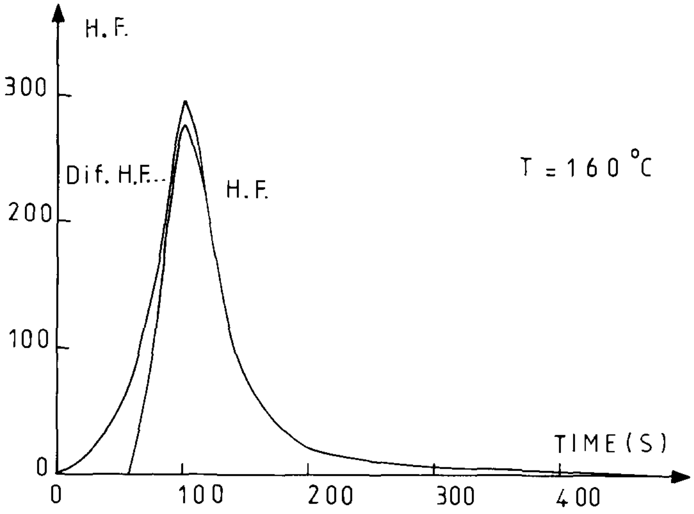

Fig. 3. Positive part of the heat flux–time history under isothermal conditions. $T = 160\,^\circ$C.

is easy from the curves shown in Fig. 3 to determine the part of the enthalpy which is lost by this technique. These values are increased with increasing temperature as shown in Table 2. The term "difference" in Table 2 characterizes the per cent enthalpy lost.

Profiles of temperature and SOC through the sample

The model gives information on the profiles of temperature and SOC as they are developed through the sample, as soon as the sample is introduced into the calorimeter. As shown in Fig. 4, ~ 1 min is necessary for the middle of the sample to reach thermal equilibrium, while high gradients are developed through the sample, especially at the beginning of the process.

Following these temperature gradients, other SOC gradients are developed through the sample. The temperature rises to a maximum value which can be much higher than the temperature of the calorimeter. This maximum value for the temperature at the middle of the sample depends on various factors. Some of these, such as the reaction enthalpy, the size of the sample and the calorimeter temperature, are of great importance.

We may conclude that heating through the sample and the reaction are expanded in an inhomogeneous way.

TABLE 2

Values of enthalpy obtained in DC

Temperature (°C)	150	160	170
Experimental enthalpy	66.9	61.3	53.4
Difference (%)	12	19.4	30

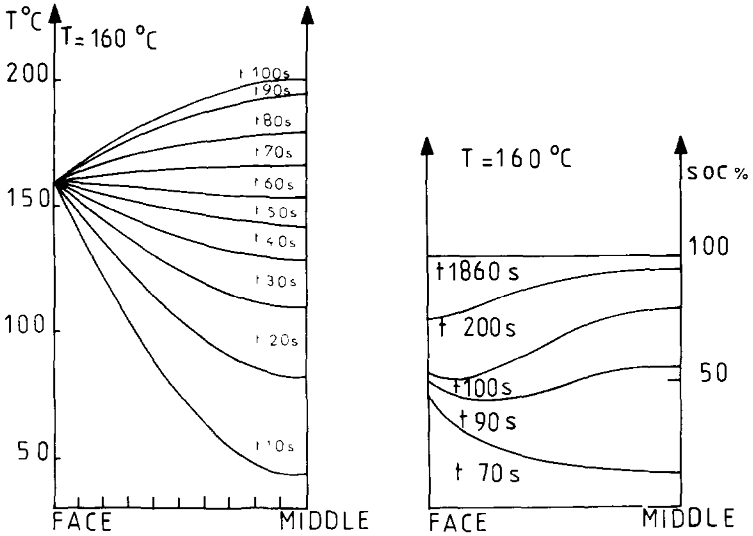

Fig. 4. Profiles of temperature and SOC developed through the sample for various times in DC. $T = 160\,°C$.

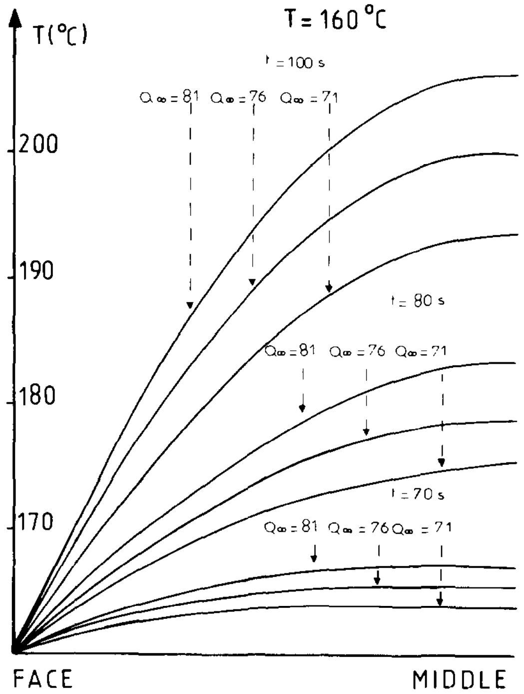

Fig. 5. Effect of a change in cure enthalpy on the profiles of temperature developed through the sample in DC at 160 °C.

Effect of a change in the enthalpy of cure

Because of the poor dispersion generally obtained from the small sample size used in DSC, irregular changes in cure enthalpy were found with time especially for the cure of epoxy resins [10].

The effect of a 5 cal g^{-1} change in the cure enthalpy around the mean value of 71 cal g^{-1} has been investigated, and the results are shown in Fig. 5 for some profiles of temperature developed through the sample at various times, and in Fig. 6 for some SOC profiles obtained for the times of interest.

There is no doubt that a change of 3% in the cure enthalpy on the above profiles is quite significant, and must be taken into account.

Calorimetry working in scanning mode

In a DSC experiment, starting with fresh, uncured material, the sample is scanned at a selected heating rate from room temperature up to a temperature at which the reaction exotherm is complete. After the sample has been cured, it is cooled to room temperature and then scanned under conditions identical to the initial scan in order to define the reference baseline.

Theoretical heat flux–time curves are obtained by using, for the constant

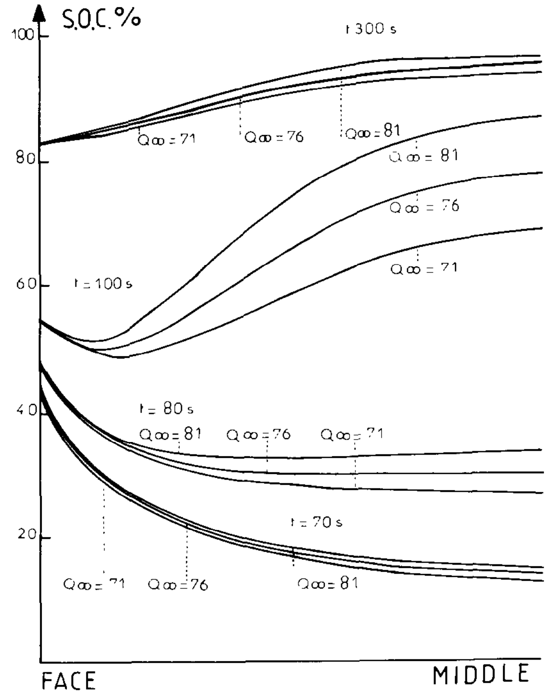

Fig. 6. Effect of a change in cure enthalpy on the profiles of SOC developed through the sample in DC at 160 °C.

rate of the kinetics of reaction, the experimental and zero values (for the reference baseline) successively.

Two parameters are considered in this paper, the heating rate and the cure enthalpy. The results obtained are concerned with the heat flux–time history, the temperature–time and state of cure–time histories.

Heat flux–time history

As shown in previous papers [6,8,11], theoretical and experimental curves are in good agreement.

The effect of heating rate on the heat flux–time (or temperature) histories may be appreciated by comparing the curves in Figs. 7–9 where the heating rate is 1, 2 and 5 °C min^{-1}, respectively. This effect is more precisely studied in Fig. 11 where the time to maximum heat flux is plotted as a function of the corresponding heating rate.

The value given to the enthalpy of cure has no effect on the shape of heat flux–time curves, as shown in Figs. 7–9. The curves obtained are of the same shape.

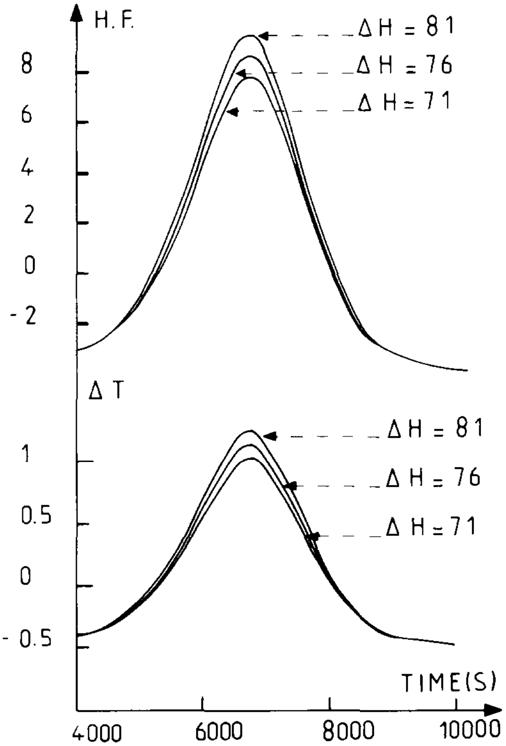

Fig. 7. Heat flux–time and temperature–time histories in DSC. Heating rate = 1 °C min^{-1}.

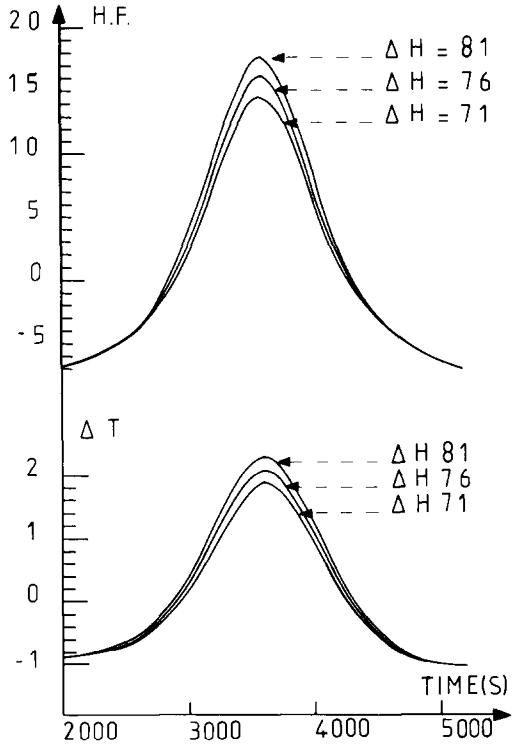

Fig. 8. Heat flux–time and temperature–time histories in DSC. Heating rate = 2° C min^{-1}.

Of course, the maximum heat flux value is proportional to the heating rate, as shown in previous studies [16] concerned with the cure of rubber of low enthalpy.

Time–temperature history

The model can determine the profiles of temperature within the sample in DSC in the same way as for DC.

The difference in the temperatures obtained at the middle of the sample and on the face (ΔT) are drawn in Figs. 7–9 as a function of the time. There is a strong similarity between these curves and the heat flux–time histories. Therefore, when no reaction occurs the value of the heat flux is negative, as well as the temperature difference ΔT; i.e., in the scanning mode, the sample is heated by the calorimeter. On the contrary, when the reaction takes place, the heat flux is emitted from the sample because of the high enthalpy of cure, and the temperature becomes higher at the middle of the sample. This is slightly different from the result obtained with rubber cure, where the temperature remained lower at the middle of the sample during the whole process [5].

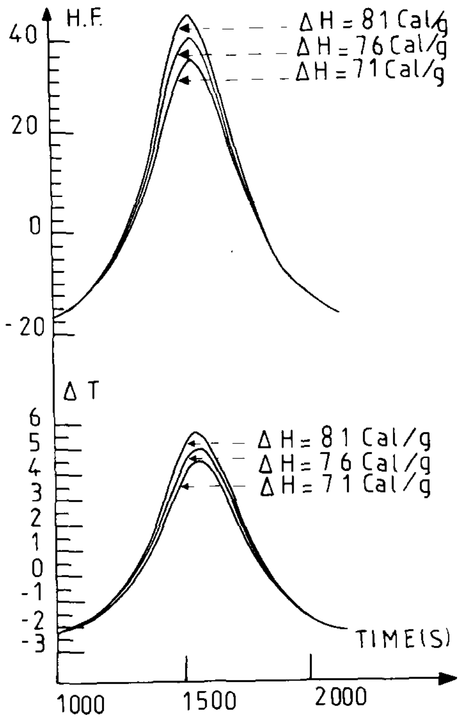

Fig. 9. Heat flux–time and temperature–time histories in DSC. Heating rate = 5° C min^{-1}.

SOC–time history

The calculated SOC–time histories are drawn in Fig. 10. The first point of

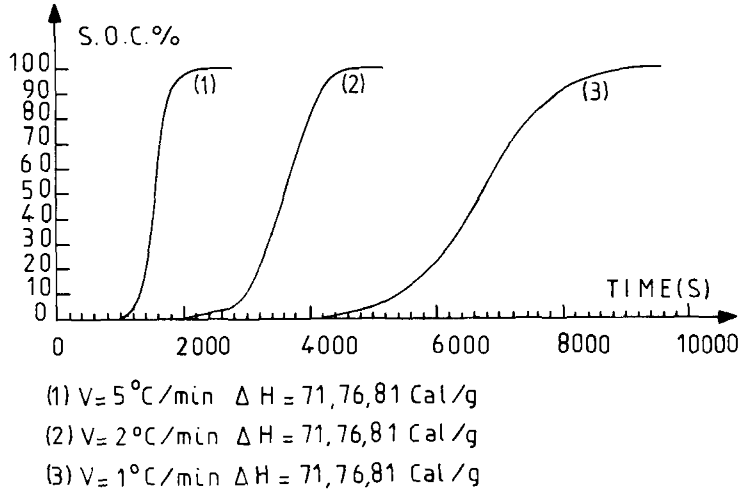

Fig. 10. SOC–time histories in DSC, for various heating rates.

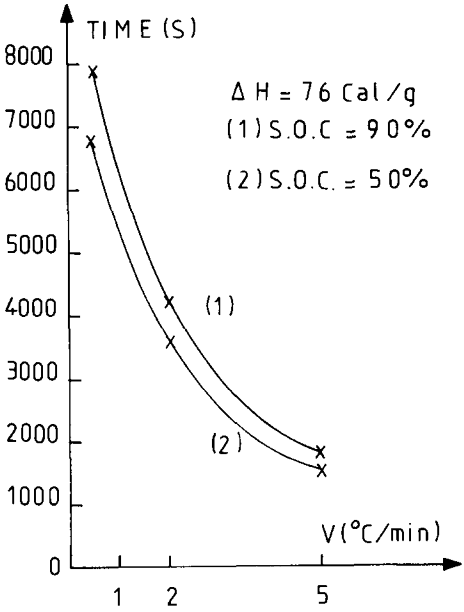

Fig. 11. Time necessary for the SOC in the middle of sample to reach a value of 50–90% as a function of the heating rate in DSC.

interest is that no significant difference is observed within the sample with the unit scale used in these curves.

A quantitative study is attempted by plotting the times necessary for the SOC to reach selected values (50 and 90%) as a function of the heating rate (Fig. 11).

CONCLUSIONS

Modelling not only gives greater insight into the processes in calorimetry, but it can also give quantitative results of interest for determining the effect of parameters.

The model described in this paper for DC and DSC techniques enables us to obtain the heat flux–time history during the process, as well as the profiles of temperature and state of cure developed at the same time within the sample.

The effect of various parameters on these profiles is determined. Various parameters are successively studied: the temperature in calorimetry working under isothermal conditions, the heating rate in the scanning mode and a change in the enthalpy of reaction. Some results concerned with either DC or DSC are of interest, especially in the case of large samples.

For instance in DC, two drawbacks must be considered because of the high gradients of temperature developed within the sample, especially during heating of the sample; the first part of the reaction cannot be obtained from experiment, and the enthalpy measured is lower than the actual enthalpy determined in scanning mode.

In DSC, the gradients of temperature developed through the sample are not as large as those developed in DC. However these gradients of temperature increase with increasing heating rate. This is certainly why the value given to the heating rate must be inversely proportional to the value of the enthalpy of reaction.

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