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ENHANCED STUDY OF DIFFERENTIAL SCANNING CALORIMETRY WITH DETERMINATION OF HEAT FLUX–TIME CURVES, PROFILES OF TEMPERATURE AND STATE OF CURE

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ABSTRACT

Differential scanning calorimetry is studied by considering the case of cure of an epoxide resin with a high enthalpy. In order to enhance this method, the heat flux due to heating of the cure reaction, and that evolving through the holder–calorimeter interface are calculated as a function of time. Simultaneously, the profiles of temperature and state of cure are determined, as they are developed through the sample during the heating. These calculations have been possible by applying our previous model taking into account heat transfer and the kinetics of heat evolved by the cure reaction. The effect of two parameters is especially considered: the heating rate, and the quality of contact between holder and the calorimeter. The higher the heating rate, the higher the gradients of temperature through the sample. Fortunately, the other, new parameter only affects the sensitivity of heat flux–time curves, it does not modify their shape, and so does not alter the following kinetic treatment.

INTRODUCTION

In this paper, a new approach to cure studies of epoxides based on differential scanning calorimetry (DSC) is explored in order to enhance this method of calorimetry. For this technique, enthalpy changes accompanying chemical events in the sample are monitored as a function of temperature, as the sample is heated at a known linear rate. The information that can be obtained from such profiles on the curing process is considered. Moreover, other complementary information is obtained by calculating the profiles of temperature developed over the whole sample and those of the state of cure, at the same time as the heat flux through the sample–calorimeter interface is measured or predicted by calculation as a function of time.

The principles of DSC measurement are described in the literature [1,2], and, therefore, need not be discussed here. However, several sources of error can arise from different factors.

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(i) In sample preparation, it is imperative that good contact is made between the cured material and the sample holder [2]. An additional remark has been previously made on the importance of the quality of contact between the holder and the calorimeter vessel [3,4].

(ii) The small sample size used in DSC necessitates that all ingredients in the sample are well dispersed; these dispersion problems can be responsible for a lack of reproducibility in the DSC curves. In our opinion, the question must always arise of how representative is a 10-mg sample or less, taken from a large batch, of the homogeneity of the batch. This is the reason why we have always preferred to use a larger sample of about 200 mg [5–7].

(iii) Because of the local heat evolved from exothermal cure reactions and the low heat conductivity through the sample [5,8], intempestive temperature gradients are developed throughout the sample. Unfortunately, the larger the sample size, the higher these gradients of temperature.

This study has needed the use of a model previously described [4,9,10] for sheets and cubes, taking into account the heat transferred by conduction through the sample, as well as the internal heat due to exothermal cure reactions. Great care has been taken over the difficult problem of the heat transfer through the calorimeter–sample interface. This model has been applied to the case at hand, with an infinite cylinder in which heat flow is radial. The kinetic parameters for cure reactions of epoxides have been assumed to be constant during the reaction, and the heat evolved by the cure reactions has been described by a single equation with a constant activation energy.

THEORETICAL

Mathematical treatment

Assumptions

(i) No flow and no molecular diffusion.

(ii) As a cylinder is used for the sample, only radial heat by conduction through the circular cross-section is considered.

(iii) Thermal parameters, such as thermal conductivity, heat diffusivity and heat capacity, are assumed constant during heating.

(iv) Kinetic parameters are kept constant, and the cure process follows a first-order reaction.

With the above assumptions, the equation of heat conduction through the cross-section reduces to

$$\rho C\frac{\partial T}{\partial t}=\frac{1}{r}\frac{\partial}{\partial r}\left(r\lambda\frac{\partial T}{\partial r}\right)+\rho\frac{\mathrm{d}Q}{\mathrm{d}t} \qquad (1)$$

where the contribution for the increase in temperature due to heat conduction and internal heat from the cure reaction can be seen.

The overall rate of cure is given by the following single equation

$$\frac{\mathrm{d}Q(r,t)}{\mathrm{d}t}=K_0(Q_\infty-Q_{r,t})\exp(-E/RT) \tag{2}$$

In the circular cross-section, the initial and boundary conditions are:

$$t=0 \quad 0\leqslant r\leqslant R_\mathrm{s} \quad T=T_r \quad \textit{sample} \tag{3}$$

$$t>0 \quad r\geqslant R_\mathrm{s} \quad T=T_\mathrm{m} \quad \textit{calorimeter}$$

$$0\leqslant r<R_\mathrm{s} \quad T=T_{r,t} \quad \textit{sample} \tag{4}$$

Numerical analysis

The general problem cannot be solved by the mathematical treatment, because of the internal heat generated by the cure reaction. The solution is given by using the following numerical method with finite differences.

Let us consider the different circles of radius r, $r+\Delta r$, $r+2\Delta r$, etc, taken on a circular cross-section perpendicular to the axis of the cylindrical sample (r being between 0 and the radius of the sample, R_s).

The heat balance is determined for the ring between $r+\Delta r/2$ and $r-\Delta r/2$, and the resulting heat balance gives

$$T_{i+1,r}=\frac{1}{M}\left[T_{i,r+\Delta r}+(M-2)T_{i,r}+T_{i,r-\Delta r}\right]$$
$$+\frac{\Delta r}{2Mr}\left[T_{i,r+\Delta r}-T_{i,r-\Delta r}\right]+\frac{1}{C}\frac{\mathrm{d}Q}{\mathrm{d}t}\Delta t \tag{5}$$

where $T_{i+1,r}$ is the new temperature at radius r after the elapse of a finite time increment Δt.

As the above equation is not determined for the middle of the cylinder ($r=0$), the following equation has been found suitable for calculating temperatures at this point

$$T_{i+1,0}=\frac{4}{M}(T_{i,\Delta r}-T_{i,0})+\frac{1}{C}\frac{\mathrm{d}Q}{\mathrm{d}t}\Delta t \tag{6}$$

For the calorimeter–sample interface, another equation has been tested

$$T_{i+1,R_\mathrm{s}}=\frac{H}{1+H}T_{i,\mathrm{m}}+\frac{1}{1+H}T_{i,R_\mathrm{s}} \tag{7}$$

by using the coefficient H evaluated by the relation

$$H=\left(\frac{\alpha_\mathrm{m}}{\alpha_\mathrm{s}}\right)^{1/2}\frac{\lambda_\mathrm{s}}{\lambda_\mathrm{m}} \tag{8}$$

In eqns. (5) and (6), M is a dimensionless number

$$M=\frac{(\Delta r)^2}{\Delta t}/\alpha_\mathrm{s} \tag{9}$$

and the increments of time and space are chosen so that $M>3$.

The heat flux (HF) transferred to the calorimeter vessel and heat flux detector is obtained by the following equation

$$\mathrm{HF} = \lambda_s \frac{T_{R_s} - T_{R_s - \Delta r}}{\Delta r} \tag{10}$$

The cure reaction is calculated by the recurrent equation

$$\left(\frac{\mathrm{d}Q}{\mathrm{d}t}\right)_{t+1} \Delta t = Q_{t+1} - Q_t = (Q_\infty - Q_t) K_0 \exp(-E/RT_t) \Delta t \tag{11}$$

with

$$Q_0 = 0 \tag{12}$$

and

$$Q_t = \sum_{i=0}^{t} \left(\frac{\mathrm{d}Q}{\mathrm{d}t}\right)_i \Delta t \tag{13}$$

EXPERIMENTAL

Calorimetry

The apparatus (DSC 111, Setaram) is used in scanning mode, by using three different values for the heating rate: 5, 10 and 20°C min^{-1}.

The aluminium holder, of rather large size (150–200 mg), is located in the calorimeter block, and the heat flux detector continuously emits a signal which is proportional to the heat transferred per unit time from the sample.

After the first cure, the sample and calorimeter are cooled to room temperature, and rescanned under the same conditions, giving the baseline which is observed in the absence of cure. This baseline allows the temperature dependence of the specific heat to be described for the cured heat.

About 150 mg of commercial epoxide resin have been used. The kinetic parameters for the cure reaction are shown in Table 1, as well as the heat transfer characteristics.

TABLE 1

Data concerned with material properties and calculations

Kinetic parameter	$n = 1$; $K_0 = 300000\ \mathrm{s}^{-1}$; $E = 15\ \mathrm{kcal\ mol}^{-1}$
Cure enthalpy	$Q_\infty = 65\ \mathrm{cal\ g}^{-1}$
Heat transfer	$\lambda = 10^{-3}\ \mathrm{cal\ s}^{-1}\ \mathrm{cm}^{-1}\ \mathrm{deg}^{-1}$; $C = 0.32\ \mathrm{cal\ g}^{-1}\ \mathrm{deg}^{-1}$; $\alpha = 25 \times 10^{-4}\ \mathrm{cm}^2\ \mathrm{s}^{-1}$
Sample dimension	$R = 0.25$ cm; 150 – 200 mg
Increments for calculation	$\Delta r = 0.025$ cm; $\Delta t = 0.05$ s; $H = 1$–20; $M = 5$

In this paper, the kinetic and heat transfer parameters are considered as constant during the cure, as assumed in the literature [11–14].

Calculation

The above explicit numerical method is available for microcomputers. Calculations were made using a Micral microcomputer (R2E, France). The increments of time and space are determined so that the modulus is higher than 3, as shown in Table 1. This value of M allows a convenient convergence for calculations.

RESULTS

Several parameters are of interest and must be studied: first, those concerned with the DSC technique, and, second, those parameters characterising the enthalpy and kinetics of the cure reaction.

In this paper, devoted to the study of the DSC technique, we will successively determine:

(1) some results simultaneously obtained by calculation with the help of our model, such as the heat flux transferred from the sample surface to the calorimeter detector, and the profiles of temperature and state of cure developed throughout the sample;

(2) the effect of heating rate must also be observed, because this is certainly the most important parameter in the DSC technique;

(3) another parameter has not been studied yet, because it is difficult to measure it at the present time, and users of DSC techniques are not usually interested in heat transfer: the quality of heat transfer through the sample–calorimeter detector interface. The present study allows one to determine the effect of this new parameter.

Determination of heat flux and profiles of temperature and state of cure

Heat flux–time curves can easily be obtained with the help of our model, as especially proved by eqn. (10). In fact, the heat flux transferred through the sample–calorimeter interface forms part of the results, because the profiles of temperature and state of cure can be obtained at the same time.

Figure 1 illustrates a typical heat flux–time curve obtained with a heating rate of 10°C min^{-1} and coefficient, H, of 20. Two curves can be seen, one determined with the rate constant, $K_0 = 3 \times 10^5$ s^{-1}, and the other with $K_0 = 0$. Of course, the first curve corresponds to the scanning with cure reaction, and the other to the rescanning obtained after cooling the apparatus to room temperature. Both these curves are very similar to the experimental ones measured under the same conditions, apart from a slight

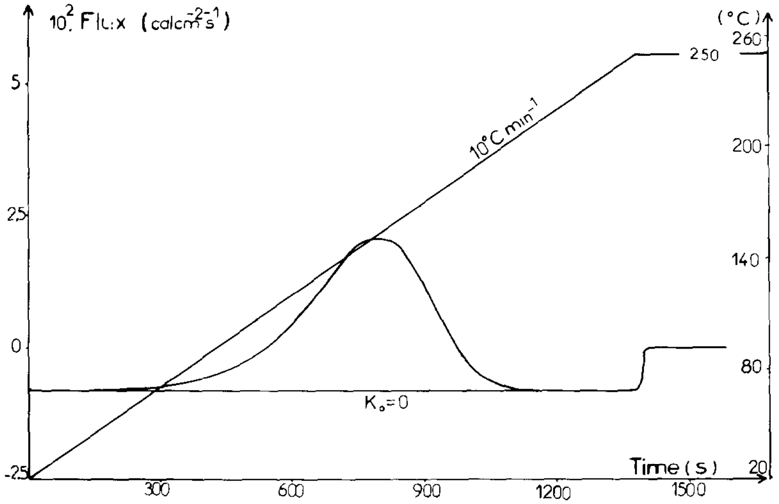

Fig. 1. Heat flux–time curve for a heating rate of 10°C min^{-1}. $H = 20$.

difference in the baselines due to a variation in the heat conductivity of the resin with temperature.

The profiles of temperature developed throughout the circular cross-section of the sample can be appreciated in Fig. 2, as they are determined under the same conditions. Because of the exothermicity of the cure reaction and the low heat transfer through the resin, temperatures inside the sample are not the same as those measured in the calorimeter vessel.

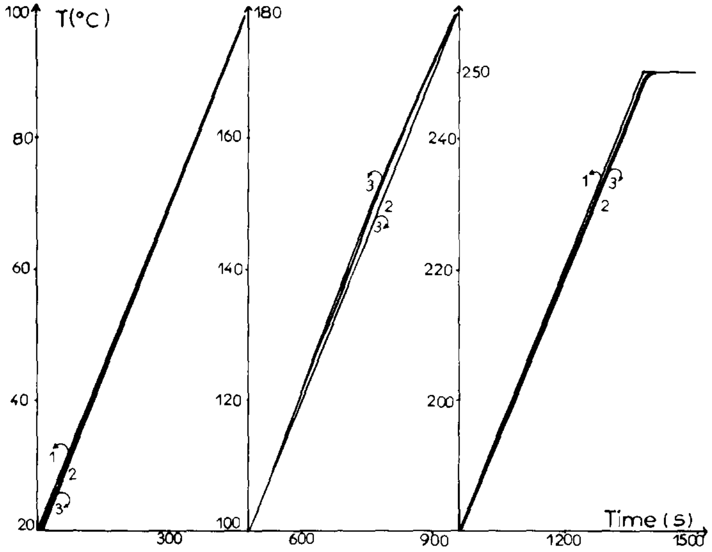

Fig. 2. Profiles of temperature through the sample while the heating rate is 10°C min^{-1}. $H = 20$. (1) Face, (2) $r = R_s/2$, (3) middle.

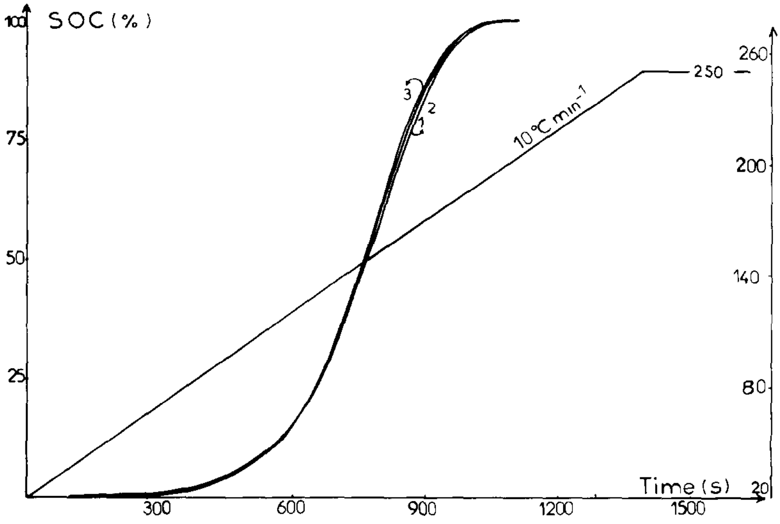

Fig. 3. Profiles of SOC through the sample. Heating rate = 10°C min^{-1}, $H = 20$. (1) Face, (2) $r = R_s/2$, (3) middle.

As shown in Fig. 2, these profiles of temperature vary with time. For times ranging from 480 to 990 s, the temperature through the sample is higher in the middle of the sample with a maximum temperature gradient of 1°C mm^{-1} at 780 s. For times lower than 480 s or higher than 990 s, temperature is lower in the middle of the sample with a maximum of the gradients, respectively, of 1.1°C mm^{-1} at 840 s, and 0.4°C mm^{-1} at 1170 s. Of course, the gradients of temperature disappeared at the inversion, at a time around 990 s.

The increase in the state of cure with time is illustrated in Fig. 3 at different places through the section of the sample. Typical inverted-S-shaped curves are shown, with higher values for the gradient of state of cure at a time around 900 s, after the maximum value of the heat flux has risen.

TABLE 2

Effect of heating rate

Heating rate	5°C min^{-1}			10°C min^{-1}			20°C min^{-1}		
Time	1170	1410	1680	630	795	936	360	450	510
Temperature (°C)	117.5	137.5	160	125	155.5	177	140	170	190
Heat flux	0.53	1.12	0.53	0.51	2.04	0.51	1.1	3.8	1.1
SOC	26	57	90	21	62	89	14.5	61	88
Sample T (°C)	118.5	138.9	160.6	126	158.1	178.4	141.8	175	192
ΔSOC	0.30	1.46	0.80	0.2	2.7	1.7	0.1	4.6	3.0
ΔT (°C)	0.50	1.4	0.6	1.0	2.6	1.4	1.8	4.9	2.0

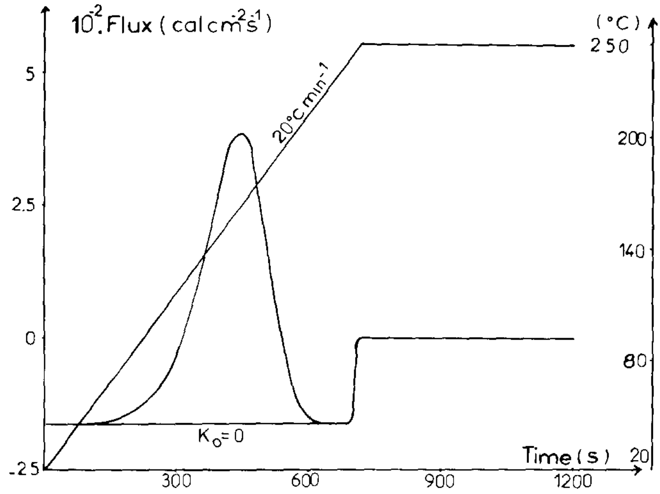

Fig. 4. Heat flux–time curve for a heating rate of 20°C min^{-1}. $H = 20$.

Some results obtained by a quantitative study are collected in Table 2 for the case with a heating rate of 10°C min^{-1}.

Effect of heating rate

As heating rate is the essential parameter for the DSC technique, we have particularly studied this parameter by considering its effect not only on heat

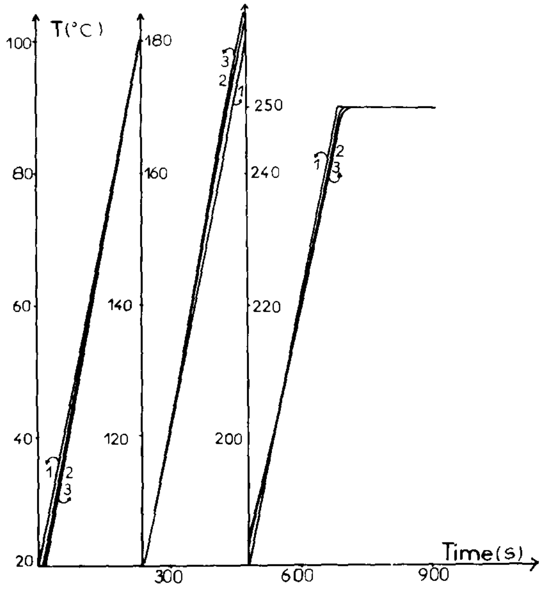

Fig. 5. Profiles of temperature through the sample. Heating rate = 20°C min^{-1}. $H = 20$. (1) Face, (2) $r = R_s/2$, (3) middle.

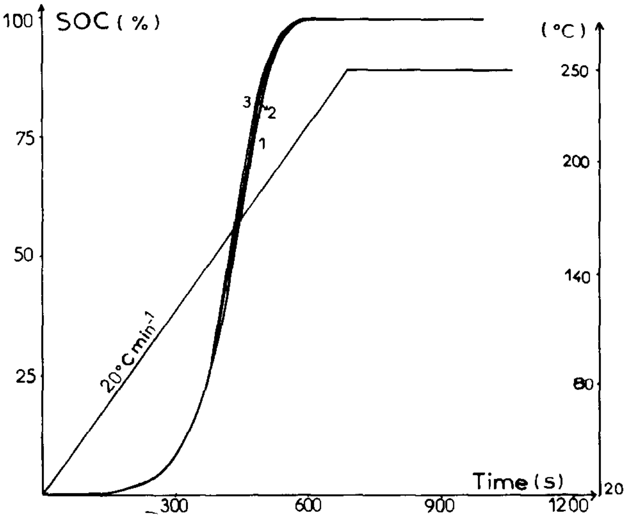

Fig. 6. Profiles of SOC through the sample. Heating rate = 20°C min^{-1}. $H = 20$.

flux–time curves, but also on the profiles of temperature and state of cure obtained at the same time.

A comparison between Fig. 1 obtained for a heating rate of 10°C min^{-1}, Fig. 4 (20°C min^{-1}) and Fig. 7 (5°C min^{-1}) gives some qualitative information on the magnitude of the effect of heating rate on the heat flux–time curves.

The effect of the value given to the heating rate on the profiles of temperature developed throughout the sample can be appreciated in Figs. 2 (10°C min^{-1}), 5 (20°C min^{-1}) and 8 (5°C min^{-1}).

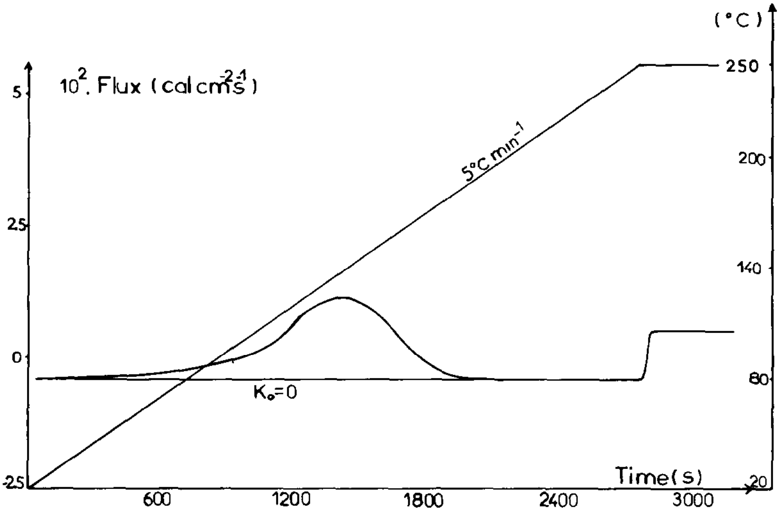

Fig. 7. Heat flux–time curve for the heating rate of 5°C min^{-1}. $H = 20$.

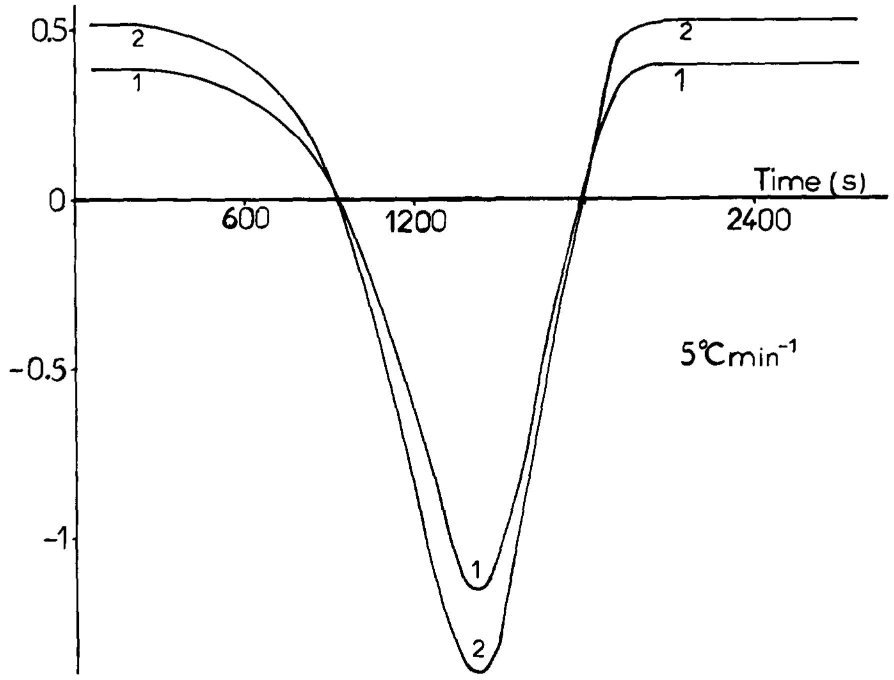

Fig. 8. Profiles of temperature through the sample. Heating rate = 5°C min^{-1}. (1) $T_{\text{face}} - T_{R_s/2}$. (2) $T_{\text{face}} - T_{\text{middle}}$.

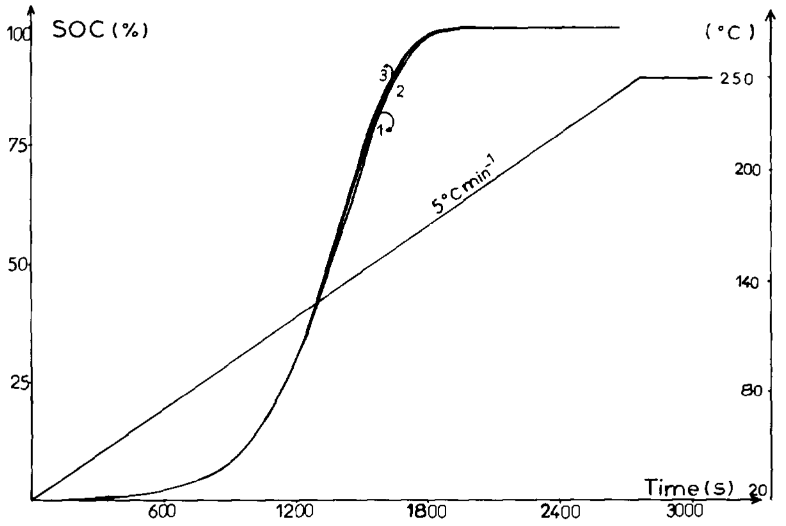

Fig. 9. Profiles of SOC through the sample. Heating rate = 5°C min^{-1}. $H = 20$. (1) Face, (2) $r = R_s/2$, (3) middle.

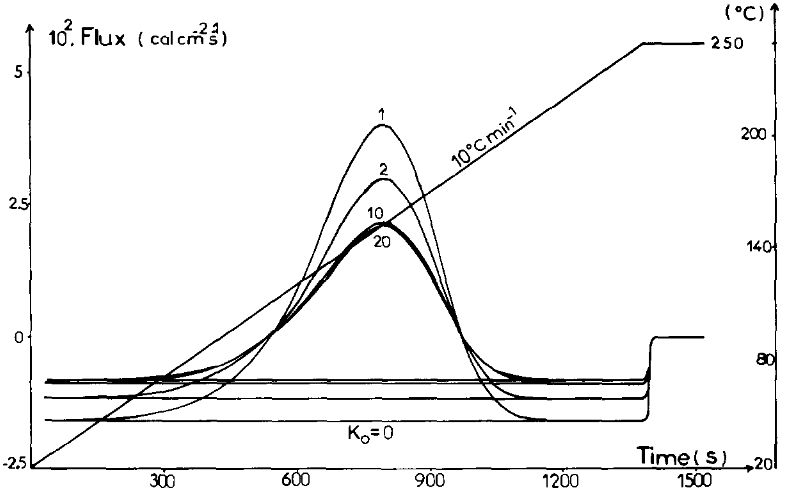

Fig. 10. Effect of H on heat flux–time curves. Heating rate = 10°C min^{-1}. $H = 1, 2, 5, 10, 20$.

The corresponding profiles of state of cure obtained with the same values of the heating rate are shown in Figs. 3, 6 and 9.

These above studies are only qualitative. An attempt has been made for a quantitative study by comparing the results in Table 2 which gives the values simultaneously obtained for heat flux, sample temperature and state of cure as a function of time and calorimeter temperature. For three different values of the heat flux (the maximum value, and the half of this maximum value) we have calculated the corresponding values for the state of cure and sample temperature, as well as the gradients of state of cure (SOC) and temperature through the sample (ΔSOC – ΔT). The sample temperature corresponds to that measured on the sample face.

Another result of interest is shown in Table 3. The maximum values for the gradients of state of cure and temperature (ΔSOC – ΔT) are indicated with regard to the time at which they are obtained.

The gradients of SOC and temperature do not reach their maximum value at the same time, but the time at which there is a maximum value for the temperature gradient is about the same time at which the heat flux is maximum.

TABLE 3

Maximum values of gradients of SOC and T

Heating rate	5°C min^{-1}	10°C min^{-1}	20°C min^{-1}
Time ($\Delta T_{\max}$) (s)	1410	800	450
$\Delta T_{\max}$ (°C)	1.42	2.62	4.91
Time ($\Delta \mathrm{SOC}_{\max}$)	1470	840	480
ΔSOC (s)	1.64	2.82	4.68

TABLE 4

Effect of H on the ratio of similarity of heat flux–time curves (10°C min^{-1})

Time (s)	660	810	912	596
$\frac{\text{HF for } H=1}{\text{HF for } H=20}$	1.93	1.93	1.93	1.93
$\frac{\text{HF for } H=2}{\text{HF for } H=20}$	1.43	1.43	1.43	1.43
$\frac{\text{HF for } H=10}{\text{HF for } H=20}$	1.04	1.04	1.04	1.04
	$\frac{1}{2}$ max HF	max of HF	$\frac{1}{2}$ max HF	20% max HF

Effect of the quality of contact between holder and calorimeter

Not having found this parameter in the literature concerned with calorimetry, we think that this paper has initiated the thought of using it for the DSC technique. The value of H, well known in chemical engineering for heat transfer through interfaces, as defined in eqn. (8), is correlated with the quality of contact between the sample holder and the calorimeter detector. Of course, the value of H depends largely on the type of calorimeter and holder. Although it is difficult to make some accurate measurements on it, we can say that a value of 20 for H corresponds to a perfect contact between iron and resin, and the value of 1 to the contact through the resin itself.

The value of H has an important effect on the magnitude of heat flux transferred to the calorimeter. The higher the value of H, the lower the sensitivity obtained for heat flux. However, the variation is not at all linear with H, and the effect is only very significant when H is low.

The value of H, fortunately, has no effect on the shape of heat flux–time curves, as shown in Table 4 where a constant ratio of similarity is found throughout the curves. So an indetermination in the value of H cannot alter the kinetic treatment of cure reactions (Fig. 10).

In the same way, the value of H has no effect on the profiles of temperature and state of cure.

CONCLUSIONS

This paper has dealt with the mathematical treatment of heat transfer in the DSC technique. With the help of chemical engineering laws and a previous model taking into account not only all heat transfer which can occur in the sample but also the kinetics of heat evolved from the cure reaction, we have coped with the problem of simultaneously obtaining heat flux and profiles of temperature and state of cure as a function of time and temperature.

A new coefficient for the DSC technique, measuring the quality of contact between the holder and calorimeter, has been introduced. Fortunately, the value found for this coefficient does not modify the shape of heat flux–time curves, and so does not interfere in the kinetic treatment of cure reactions.

Of course, the higher the heating rate, the higher the profiles of temperature developed through the sample during the cure. This fact of interest improves the understanding on this technique, but it also makes a further investigation necessary in order to develop a new method able to determine accurate kinetic parameters under these conditions.

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