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MODELIZATION OF THE DSC TECHNIQUE BY CONSIDERING HEAT TRANSFER AND KINETICS OF REACTION IN THE CASE OF RUBBER CURE

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ABSTRACT

The low-enthalpy rubber cure reaction is studied by using differential scanning calorimetry with a sample of about 150 mg. The model described can simultaneously give heat flux–time curves, and the profiles of temperature and state of cure developed through the rubber. This model takes into account not only the kinetics of heat evolved from the cure reaction, but also the heat transfer through the rubber and calorimeter–rubber interface. A new parameter is introduced, qualifying the quality of contact between calorimeter and sample. This parameter affects sensitivity of the heat flux, but not the position and shape of the heat flux–time curve. Theoretical heat flux–time curves are in good agreement with the experimental curves. The effect of heating rate has also been studied. An increase in the heating rate is responsible for an increase in peak height of the corresponding heat flux–time curve, and an increase in the profile of temperature and state of cure developed through the sample.

INTRODUCTION

Differential scanning calorimetry (DSC) has very often been used for characterising the cure process of rubber [1,2]. The enthalpy change accompanying the cure reaction in the sample is monitored; the result is a profile of the rate of enthalpy change as a function of temperature while the calorimeter is heated at a known linear rate. Information obtained from such profiles on the cure process is of interest, but it must be emphasised that some limitations in experimental technique and data interpretation occur with this technique, as with other thermoanalytical methods.

Several sources of error can arise from different factors.

(i) A good contact must be made between the cured rubber and the sample holder [2], and we have noticed the importance of the quality of contact between the holder and the calorimeter vessel [3,4].

(ii) The applied temperature is the set calorimeter temperature and not the true rubber temperature during cure, because of local heating arising

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from exothermic reactions and low heat transfer through the rubber [5,6]. Moreover, intempestive gradients of temperature are developed throughout the rubber sample during cure.

(iii) Because of the small size used in DSC, all ingredients in the rubber compound must be well dispersed; dispersion problems are responsible for a lack of reproducibility in DSC curves. The question very often arises of how representative a 5–10 mg sample is, taken from a large batch, of the homogeneity of the batch. This is the reason why it is sometimes preferred to use larger samples of 100–200 mg [5–7]. Unfortunately, however, the larger the sample size, the higher the gradients of temperature developed through the rubber during cure.

Our purpose in this work is to study all events occurring throughout the rubber sample during cure by DSC. Thus, the heat flux transferred through the sample–calorimeter interface has been calculated during cure, as well as profiles of temperature and state of cure obtained throughout the rubber.

The problem has been solved by using a model previously described for determining profiles of temperature and state of cure developed through rubber sheets pressed into mold slabs [6–8]. The temperature and extent of reaction (SOC) are functions of both time and position through the rubber, and can be determined by the balance of internal heat from the cure reaction, heat conduction through the sample and heat exchange with the surroundings. This model has been developed in the case at hand, with a cylindrical sample submitted to heating in the calorimeter cell. The problem has been solved by applying a numerical method with finite differences to this cylindrical sample. Although sulfur-vulcanization of rubber is a complex chemical process [9,10], the overall result, by considering heats of reaction, has been described by a first-order reaction with a single activation energy [5,11].

In this paper, two parameters concerned with the DSC technique are especially studied: quality of contact with the sample holder, and the heating rate of the microcalorimeter. The effect of these parameters on heat flux–time curves and profiles of temperature and state of cure is evaluated.

THEORETICAL

Assumptions

Several basic assumptions are made in this work.

(1) The sample is cylindrical in shape with a circular cross-section of 5 mm in diameter. Heat flow is considered as radial, the longitudinal heat transfer being neglected.

(2) The quality of contact between the sample holder and the calorimeter detector is discussed. As the rubber is elastic, contact between the rubber and holder is supposed to be perfect.

(3) Although the kinetic parameters for the overall reaction have been found to vary a little, especially at the end of the cure reaction [12,13], they are assumed to be constant throughout the reaction in this paper.

(4) Because of the low effect of variation in thermal properties with temperature on the cure process [4], they are considered to be constant during heating.

Fundamental equations

The equation of transient heat conduction through the cylindrical cross-section of a rubber sample is expressed as follows

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

The overall rate of cure is given by the simple first-order reaction

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

Initial and boundary conditions are

$$t = 0 \quad 0 \leqslant r \leqslant R_\mathrm{s} \quad T = T_\mathrm{r} \quad \text{rubber space} \tag{3}$$

$$t > 0 \quad r \geqslant R_\mathrm{s} \quad T = T_\mathrm{m} \quad \text{oven space} \tag{4}$$

$$0 \leqslant r < R_\mathrm{s} \quad T = T_{r,t} \quad \text{rubber space}$$

Numerical analysis

Equations (1) and (2) cannot be solved by a mathematical treatment, because of internal heat from the cure reaction and the quality of contact at the oven–holder interface. We have therefore used an explicit method with finite differences.

Let the circular cross-section be divided into several circles of radius having the successive values r, $r + \Delta r$, $r + 2\Delta r$, with Δr being a constant radius increment. On the circle of radius r, the temperature at time $(i + 1)\Delta t$ is a function of the temperature at the preceding time $i\Delta t$ on circles of radius r, $r - \Delta r$ and $r + \Delta r$, as follows

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

On the sample face, the heat balance allows one to write

$$T_{i+1,R_\mathrm{s}} = \frac{H}{1+H} T_{i,\mathrm{m}} + \frac{1}{1+H} T_{i,R_\mathrm{s}} \tag{6}$$

where the coefficient H characterizing the quality of contact between the mold and holder, is defined by the equation [14]

$$H = \left(\frac{\alpha_m}{\alpha_s}\right)^{1/2} \frac{\lambda_s}{\lambda_m} \qquad (7)$$

In the middle of the sample, eqn. (5) is not valid, and the temperature is calculated with the following equation

$$T_{i+1,0} = \frac{4}{M}(T_{i,\Delta r} - T_{i,0}) + \frac{1}{C}\frac{dQ}{dt}\Delta t \qquad (8)$$

The modulus M is dimensionless

$$M = \frac{(\Delta r)^2}{\Delta t}\frac{1}{\alpha_s} \qquad (9)$$

It is not easy to obtain the heat flux (HF) between the heat flux detector of the calorimeter and the sample face, so we have calculated HF emitted through adjacent circles in the rubber of radius R_s and $R_s - \Delta r$

$$\mathrm{HF} = \lambda_s \frac{T_{R_s} - T_{R_s - \Delta r}}{\Delta r} \qquad (10)$$

The heat evolved by the cure reaction during the incremental time Δt is obtained with the recurrent relation

$$\left(\frac{dQ}{dt}\right)_{i+1}\Delta t = Q_{i+1} - Q_i = (Q_\infty - Q_i)K_0 \exp - \frac{E}{RT_i}\Delta t \qquad (11)$$

where Q_i is expressed as follows

$$Q_0 = 0 \text{ and } Q_i = \sum_{i=0}^{i}\left(\frac{dQ}{dt}\right)_i \Delta t \qquad (12)$$

EXPERIMENTAL

Description of the technique and apparatus

The DSC 111 (Setaram, Lyon, France) used in this work is a heat-flux calorimeter with a temperature programming facility. The cylindrical sample is located in an experimental vessel; the vessel is placed in the calorimeter block which functions as a heat sink. The temperature of this block is controlled. A heat flux detector, consisting of thermocouples, connects the vessel thermally to the block, so that the vessel temperature is always as close as possible to that of the block.

The calorimeter monitors the heat flux between the system and the block. The external diameter of the holder is 5 mm, and the internal diameter of the block is 5.1 mm.

TABLE 1

Parameters concerned with the rubber

Cure enthalpy: 10 cal g^{-1}
Kinetic: $n=1$; $K_0 = 3\times10^9$ s^{-1}; $E = 25400$ cal mol^{-1}
Sample: 150 mg; $R_s = 0.25$ cm
Heat transfer: $\lambda = 55\times10^{-3}$ cal s^{-1} cm^{-1} K^{-1}; $c = 0.37$ cal g^{-1} K^{-1}; $\alpha = 10^{-3}$ cm^2 s^{-1}

TABLE 2

Parameters for calculation

Radius = 0.25 cm; number of sides = 10
Increments: $\Delta r = 0.025$ cm; $\Delta t = 0.2$ s; $M = 3.12$; $H = 1$

The size of the sample is between 100 and 200 mg, depending on the density of the material. For rubber it is about 150 mg.

Materials

A rubber powder–sulfur compound is used in the sample. Sulfur (2% in weight of the mixture) is preliminarily mixed with the 50–250 μm grain-size rubber. Kinetic parameters for the cure reactions, as determined previously [5], are shown in Table 1, as well as the heat-transfer parameters.

Calculation

Heat flux emitted through the sample–calorimeter interface, as well as temperatures and state of cure developed through the cross-section of the sample, are calculated by using the above model. The parameters used for numerical analysis are shown in Table 2.

RESULTS AND DISCUSSION

Some parameters are of interest, particularly the heating rate characterizing the DSC technique, and the quality of heat transfer through the sample–calorimeter detector.

Effect of heating rate on heat flux–time curves

Figure 1 shows the heat flux–time curves calculated for the cure of the rubber sample described in Table 1 with a heating rate of 2°C min^{-1}. One

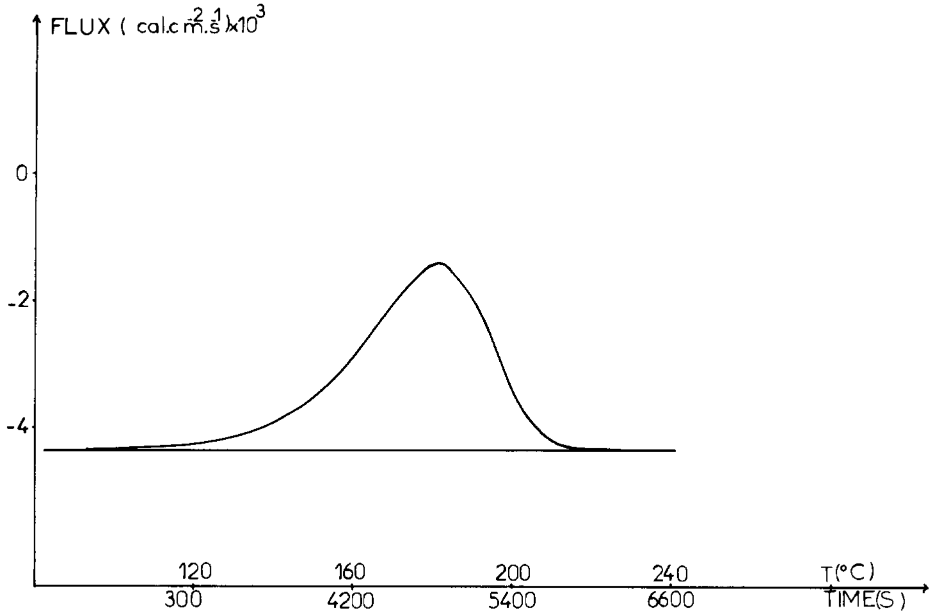

Fig. 1. Heat flux–time curve for a heating rate of 2°C min^{-1}.

curve obtained with the rate constant $K_0 = 3 \times 10^5$ s^{-1} corresponds to the first scanning with the cure reaction, while the other curve with $K_0 = 0$ corresponds to the rescanning obtained after cooling the apparatus and sample to room temperature. In the present case, the temperature is programmed from room temperature (30°C) to about 250°C. Both these curves are much alike the experimental ones determined under the same conditions, with only a slight difference in slope of the baseline obtained with $K_0 = 0$. This difference is due to a variation in heat transfer parameters of rubber with temperature.

The effect of heating rate may be appreciated by comparing the heat flux–time curves shown in Fig. 2 (5°C min^{-1}), Fig. 3 (10°C min^{-1}) and Fig. 4 (20°C min^{-1}).

Of course, the higher the heating rate, the shorter the time necessary for completion of the reaction. Some other results of interest are collected in Table 3.

Thus, an increase in heating rate is responsible for the following facts.

(1) An increase in the value of maximum of heat flux, corresponding to a higher sensitivity, the area of the exotherm peak measuring cure enthalpy being about the same.

(2) A decrease in time at which the heat flux reaches its maximum value, as well as that of completion of reaction.

(3) An increase in temperature for which the heat flux is maximum.

(4) A decrease in width of the exothermal peak determined at the half height expressed in minutes.

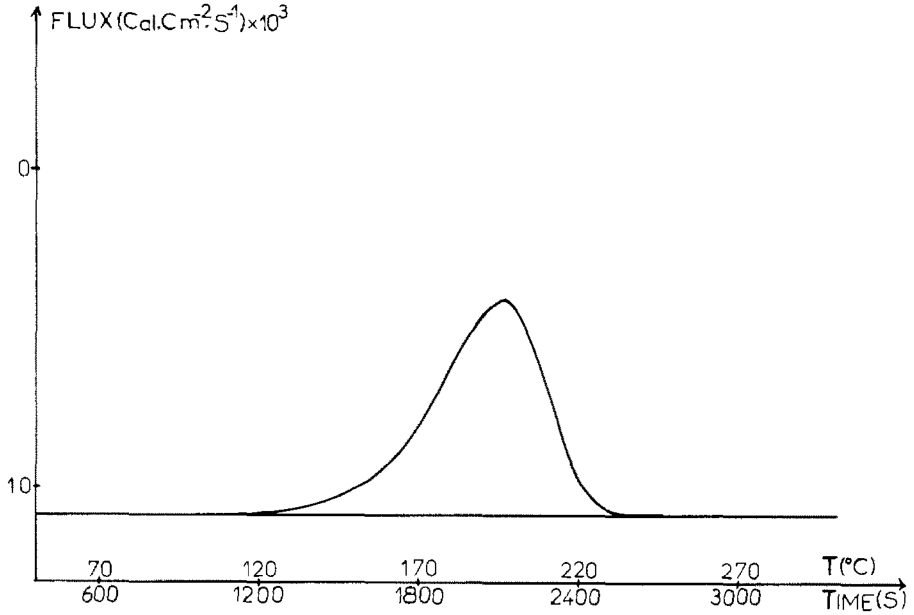

Fig. 2. Heat flux–time curve for a heating rate of 5°C min^{-1}.

The height of the peak corresponding to the heat flux–time curves is proportional to the 0.9th law of the heating rate, while the area of the peak does not depend on the value of this heating rate.

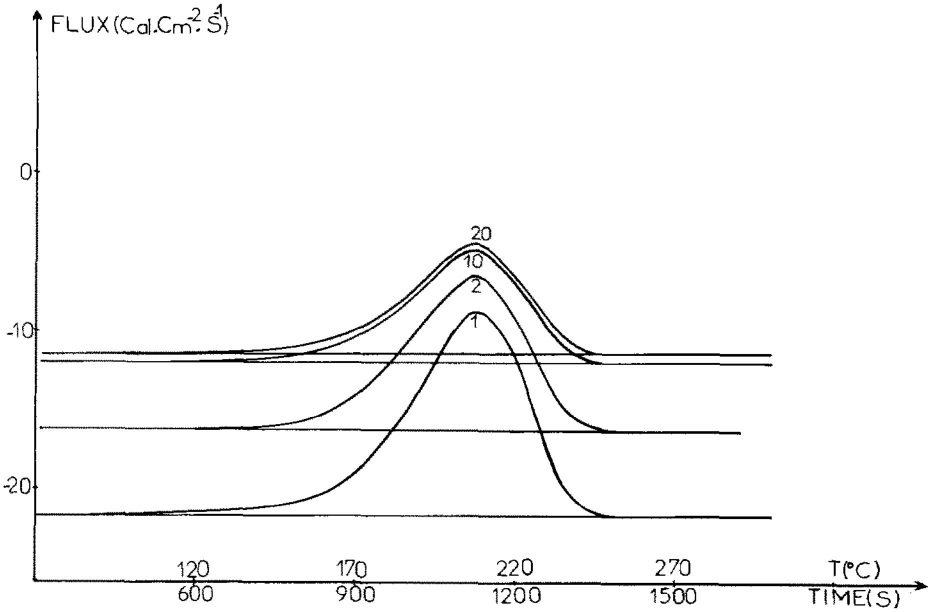

Fig. 3. Heat flux–time curves for a heating rate of 10°C min^{-1}; effect of $H = 1$, 5, 10 and 20.

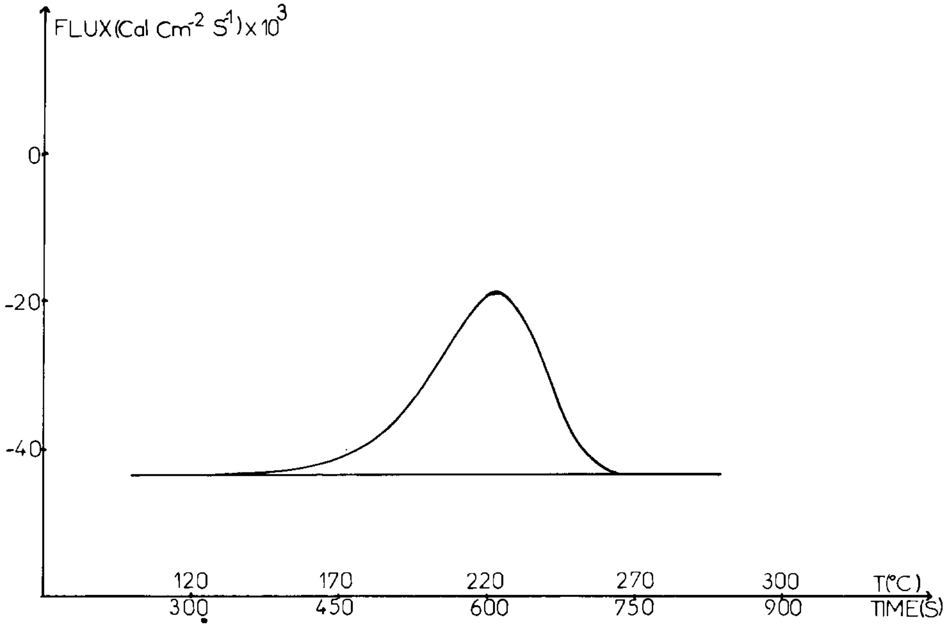

Fig. 4. Heat flux–time curve for a heating rate of 20°C min^{-1}.

TABLE 3

Heating rate and heat flux–time curves

Heating rate (°C min^{-1})	2	5	10	20
Heat flux (cal cm^{-2} s^{-1} × 10^{3})	3.9	6.85	11.5	21.1
Time for max HF (s)	4860	2124	1125	607
Tem. for max HF (°C)	180	197	207	222
ΔT at half height (°C)	36	39.5	42	53.5
Δt at half height (s)	1080	474	252	120

Effect of heating rate on profiles of temperature

An important part of this work is devoted to the determination of profiles of temperature and state of cure developed through the rubber sample during cure reaction.

Profiles of temperature developed throughout the circular cross-section of the sample can be appreciated in Figs. 5–8 for different heating rates.

While the calorimeter temperature is programmed, there is a retardation in temperature inside the sample with regard to that of the calorimeter. As the heating rate for the calorimeter is constant, the above retardation is almost constant as shown in Figs. 5–8, when neither a change reaction nor thermal properties occurs. However, because of internal heat due to the cure reaction, this retardation in temperature may be reduced if heating is slow,

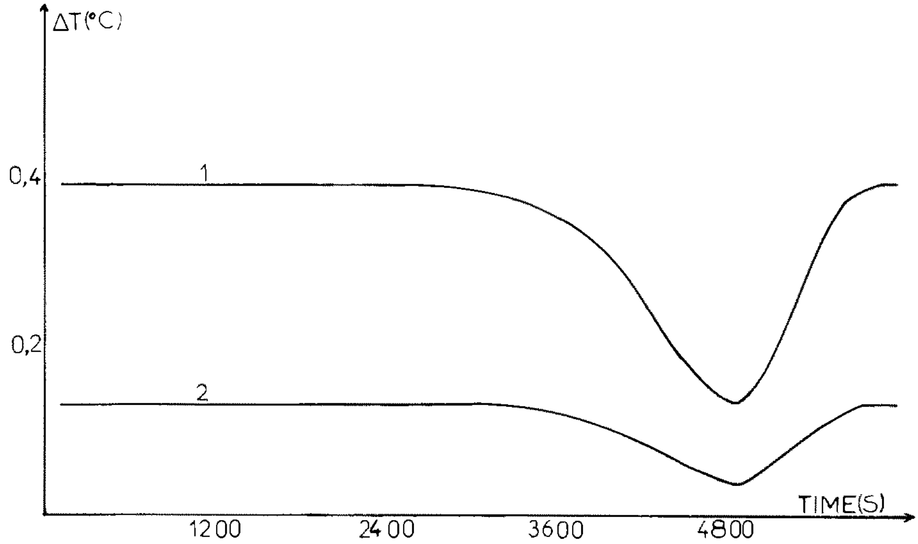

Fig. 5. Profiles of temperatures through the rubber. Heating rate = 2°C min^{-1}; (1) $T_{\text{face}} - T_{\text{middle}}$; (2) $T_{R_s/2} - T_{\text{middle}}$.

as shown in Table 4 ($\Delta T = T$ for $r = (R_s/2) - T$ for $r = 0$). This retardation could even be negative, the temperature being higher at the middle of the sample, when the heat of cure reaction is high enough, as obtained for epoxide cure with enthalpy ranging from 60 to 80 cal g^{-1} [14].

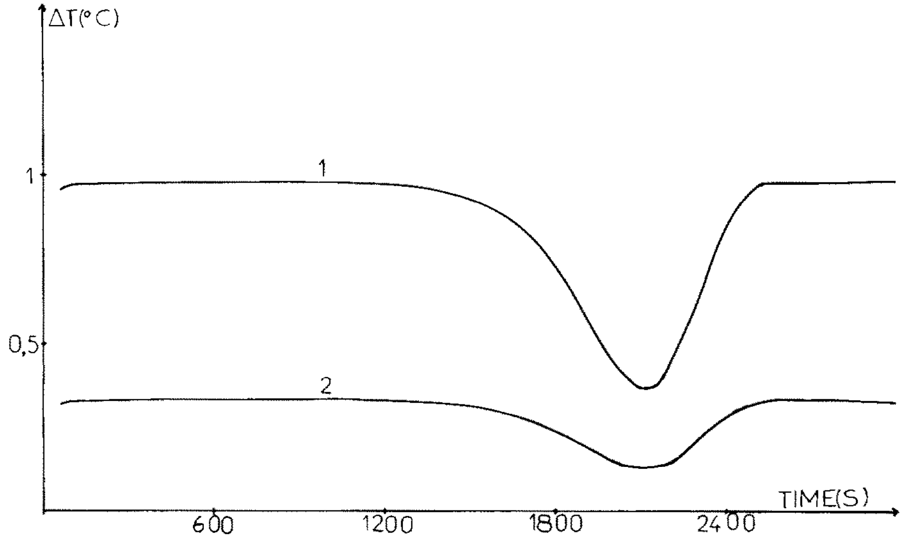

Fig. 6. Profiles of temperatures through the rubber. Heating rate = 5°C min^{-1}; (1) $T_{\text{face}} - T_{\text{middle}}$; (2) $T_{R_s/2} - T_{\text{middle}}$.

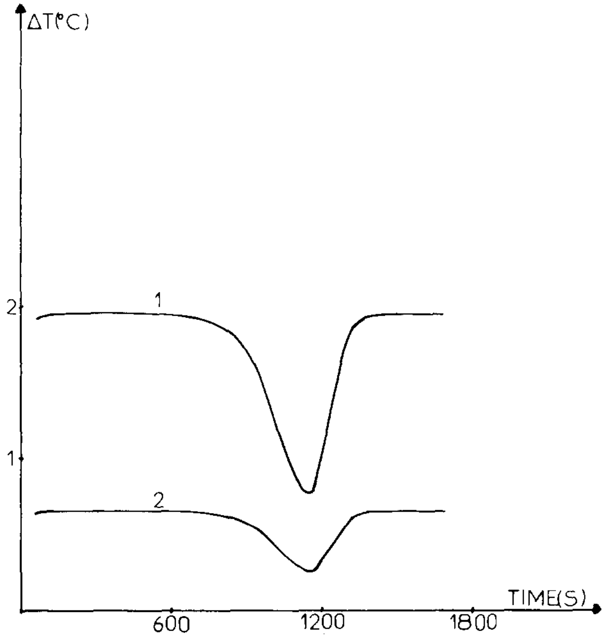

Fig. 7. Profiles of temperatures through the rubber. Heating rate = 10°C min^{-1}; (1) $T_{\text{face}} - T_{\text{middle}}$; (2) $T_{R_s/2} - T_{\text{middle}}$.

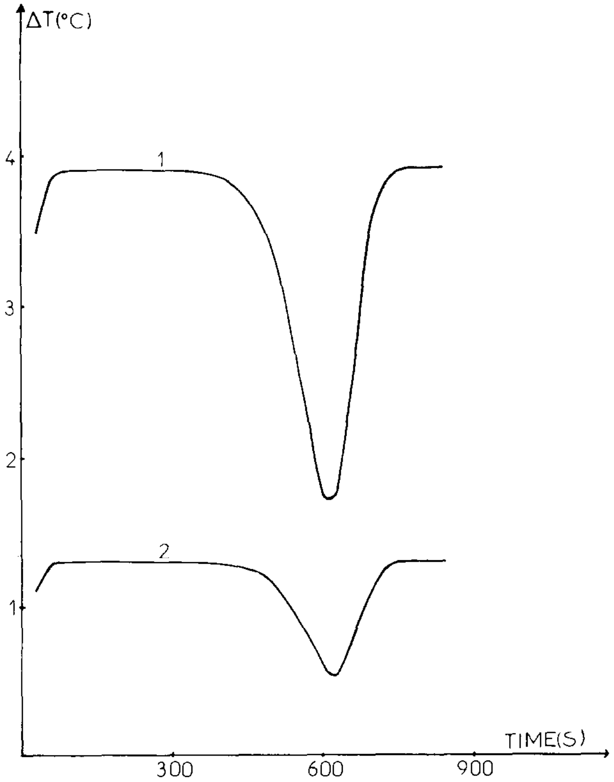

Fig. 8. Profiles of temperatures through the rubber. Heating rate = 20°C min^{-1}; (1) $T_{\text{face}} - T_{\text{middle}}$; (2) $T_{R_s/2} - T_{\text{middle}}$.

TABLE 4

Effect of heating on the profiles of temperature

Heating rate (°C min^{-1})	2	5	10	20
Mean ΔT (°C)	0.12	0.31	0.64	1.3
ΔT min (°C)	0.04	0.13	0.26	0.55
Time for ΔT min (s)	4800	2100	1140	630

A point of interest is shown in Table 4 and Figs. 4–8 concerned with these profiles of temperature. The change in the profiles of temperature developed through the rubber is maximum when the rate of internal heating is maximum.

Effect of the heating rate on the profiles of state of cure

As the temperature is not the same throughout the cross-section of the sample, the rate of cure reaction must vary throughout the sample, and some profiles of state of cure can be obtained. These profiles of state of cure have been calculated, as shown in Figs. 9–12 for the different heating rates. We have also determined the difference in values of state of cure as they are obtained in two positions taken for $r = 0$ and $r = R_s/2$ (Table 5).

Thus, if state of cure is considered, reaction in the sample is heterogeneous, and the difference in state of cure determined at the above cited

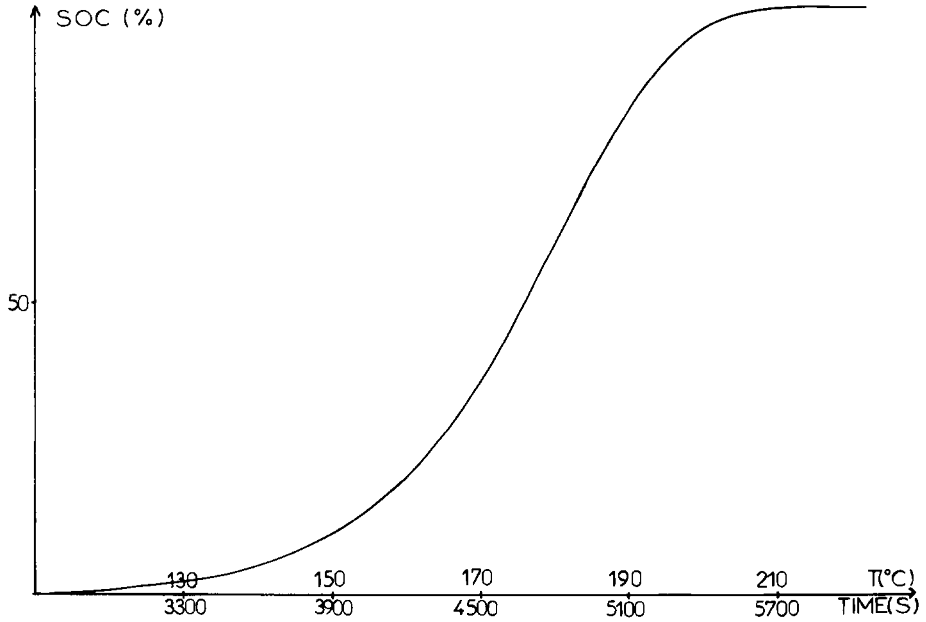

Fig. 9. Profiles of state of cure through the rubber. Heating rate = 2°C min^{-1}.

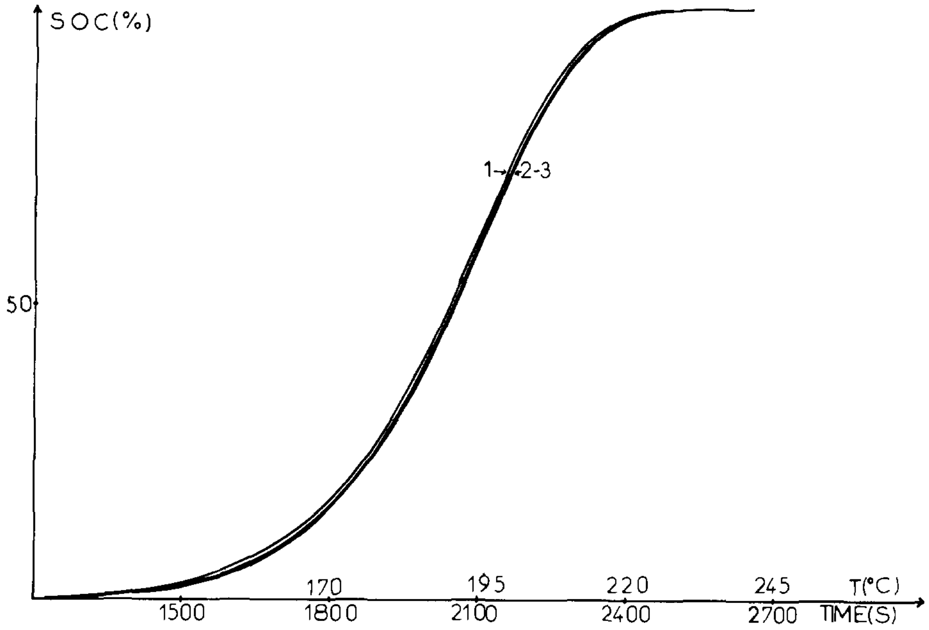

Fig. 10. Profiles of state of cure through the rubber. Heating rate = 5°C min^{-1}; (1) on sample face; (2) for $r = R_s/2$; (3) for $r = 0$.

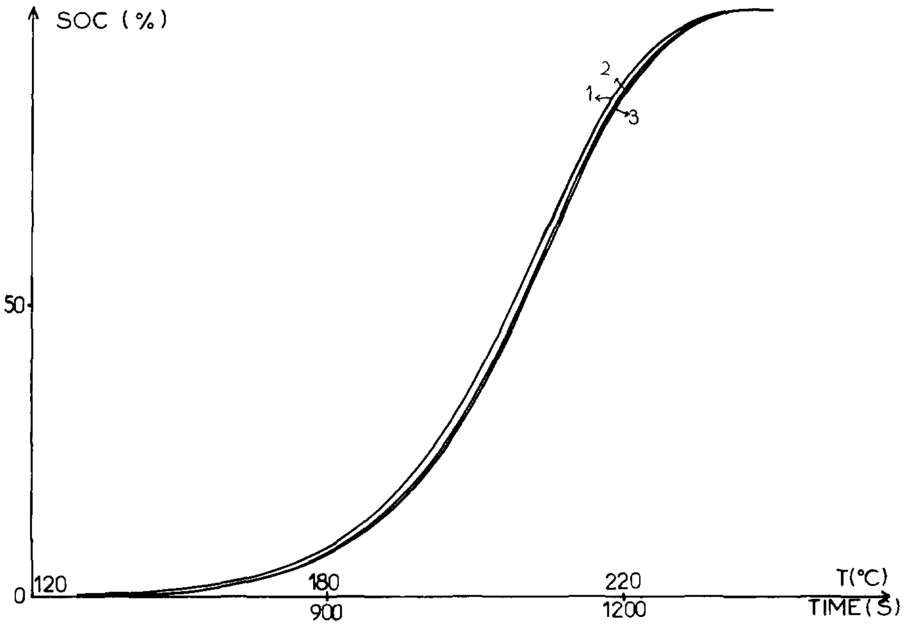

Fig. 11. Profiles of state of cure through the rubber. Heating rate = 10°C min^{-1}; (1) on sample face; (2) for $r = R_s/2$; (3) for $r = 0$.

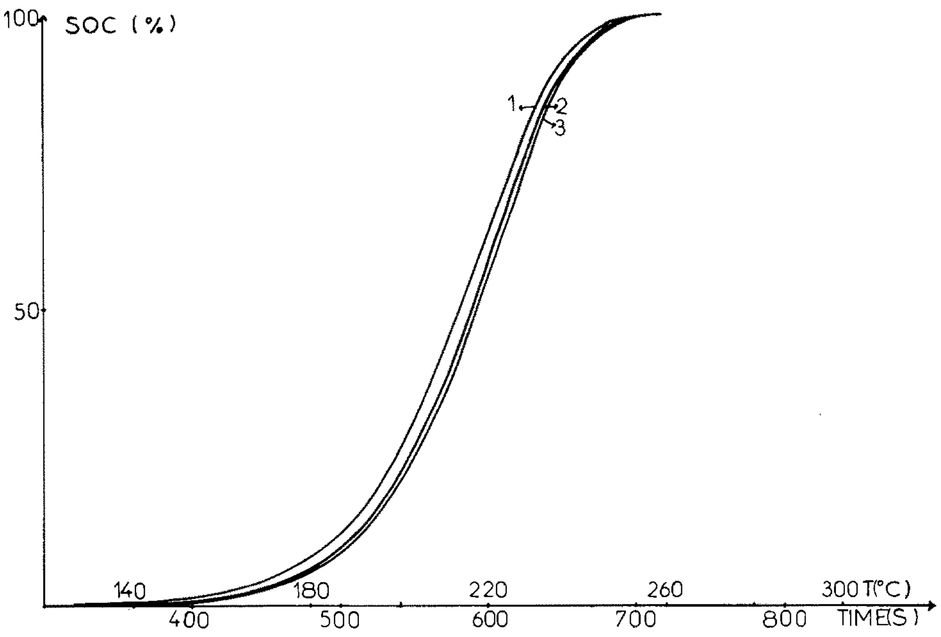

Fig. 12. Profiles of state of cure through the rubber. Heating rate = 20°C min^{-1}; (1) on sample face; (2) for $r = R_s/2$; (3) for $r = 0$.

TABLE 5

Effect of heating rate on the profiles of SOC

Heating rate (°C min^{-1})	2	5	10	20
ΔSOC max (%)	0.73	1.8	3.6	5
Time for ΔSOC max (s)	4620	2040	1080	6.0
ΔSOC at HF max	0.65	1.7	3.2	7

places reaches a maximum value when the heat flux is not far from its maximum value.

Effect of the quality of contact between the calorimeter and the sample

The quality of contact between the sample and the calorimeter is defined by the value of the coefficient *H* shown in eqn. (7). It is still difficult to make accurate measurements for this coefficient, because of the small empty space between the calorimeter and holder. However, a value of 20 for *H* corresponds to perfect contact between iron and rubber, and the value of 1 to contact through the rubber itself. As shown in Fig. 3 for a heating rate of 10°C min^{-1}, the effect *H* on the value determined for the heat flux transferred to the calorimeter is not negligible. The higher the value of *H*, the lower the sensitivity obtained for the heat flux. The variation in sensitivity of the calorimeter is not linear with H value, and the effect of H becomes significant when its value is low.

Although the value of H is of interest for the sensitivity of the calorimeter, it has no effect on the shape of heat flux–time curves, and profiles of temperature and state of cure. So an indetermination in the value of the coefficient H does not provoke any alteration in kinetic treatment of cure reactions.

CONCLUSIONS

A calculation has been made in this paper for the DSC technique in the case of rubber cure of low enthalpy. The model used for this calculation takes into account not only the kinetics of heat evolved from the cure reaction, but also all heat transfers which occur during the process: conduction through the sample followed by heat transfer through the calorimeter–sample interface.

Several results of interest have been simultaneously obtained: heat flux–time curves, and profiles of temperature and state of cure as a function of time and space in the sample. The heat flux–time curves obtained by calculation correspond well with the experimental ones in shape and position.

A new parameter for DSC techniques is shown, measuring the quality of contact between the holder and the calorimeter. Fortunately, the values tested for this coefficient do not modify the shape and position of heat flux–time curves, and so do not modify the kinetic parameters. However, this parameter is found to be of importance for the sensitivity of the calorimeter concerned with heat flux, and this point is of interest for studies of rubber cure with low enthalpy.

The effect of heating rate on the DSC technique has been especially studied; an increase in heating rate is responsible for the following factors.

(1) An increase in sensitivity for measuring heat flux, and a decrease in width of heat flux peak, the area of the peak being about constant.

(2) An increase in heterogeneity in the sample, due to the development of profiles of temperature and state of cure through the rubber mass.

The above-cited factors provoke some problems for determining accurate parameters of the kinetics of cure reaction by using the DSC technique. However, knowledge obtained on profiles of temperature will help us to make further investigations in order to develop a method able to give accurate kinetic parameters.

LIST OF SYMBOLS

ρ	density of rubber
C	specific heat of rubber
λ_s	thermal conductivity of rubber
λ_m	thermal conductivity of metal
T	temperature
t	time
R	radius in cross-section of cylindrical sample
r	radius of circumference in cross-section
Q_∞	enthalpy of cure reaction
$Q_{r,t}$	enthalpy evolved up to time t at position r
Δt	finite increment in time
Δr	finite increment in radius
a	thermal diffusivity
n	order of overall cure reaction
K_0	rate constant of reaction
E	energy of activation

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