STUDY OF HEAT FLUX AND PROFILES OF TEMPERATURE AND STATE OF CURE OBTAINED IN AN ISOTHERMAL CALORIMETER WITH RUBBER CURE OF LOW ENTHALPY

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ABSTRACT

Although the cure of rubber is not very exothermic (10 cal g^{-1}), important temperature gradients are developed through the sample when it is submitted to heat inside the calorimeter. Calorimetry studies have been conducted under isothermal conditions with a cylindrical sample of between 100 and 200 mg. The profiles of temperature and state of cure developed through the cross-section of the sample have been calculated, as well as the heat flux obtained through the sample–calorimeter interface. The heat flux–time curves calculated are in agreement with the experimental ones. Data concerned with the kinetics of heat evolved by the overall reaction and heat transfer by conduction are used for these calculations. Calculations have been done with the help of an explicit numerical method with finite differences. The method described here enables one to collect simultaneously some complementary information on heat flux (the rate of reaction) along with profiles of temperature and state of cure.

INTRODUCTION

In the past decade, the development of highly sensitive and reliable thermoanalytical methods, such as differential thermal analysis (DTA), differential scanning calorimetry (DSC) and isothermal calorimetry (DC), has presented a new approach to the accurate and rapid determination of temperature (DTA) or energy changes (DSC–DC) associated with a thermal event. In DSC and DC, the sample is subjected to a known heating program, either in the scanning mode or under isothermal conditions, and the energy changes arising from thermal events in the sample are monitored as a function of temperature (DSC) or time (DC). The changes are measured with respect to an inert reference which is simultaneously subjected to the same heating program.

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Although the accelerated sulfur vulcanization of unsaturated elastomers is a very complex chemical process involving numerous simultaneous and consecutive reactions [1,2], thermal analytical procedures have been used with success for studying the exothermicity of overall reactions. In the first studies on elastomer vulcanization [3,4] no exothermicity in the unaccelerated cure was reported at sulfur levels below 6%, but this fact was due to the insensitivity of the apparatus. More recently, DSC was proved to provide useful information on the cure characteristics of typical elastomer formulations [5–8], notably the position of the exotherm and the magnitude of the exothermic enthalpy. DC curves obtained at different temperatures were found to be convenient for determining the kinetics of the overall cure reaction of sulfur–rubber compounds [9,10].

The purpose of this work is to study all the events occurring through the sample mass during the cure in the calorimeter cell. Since polymers exhibit a low thermal conductivity and the curing reaction is exothermic, the temperature and rate of reaction can vary considerably within the curing mass. Therefore, the extent of reaction is a function of time as well as position through the sample. It can be determined by the balance of internal heat generation from the curing reaction, heat conduction through the sample and heat exchange with the surroundings [11,12]. Our model, previously used for calculating the profiles of temperature and state of cure obtained through rubber sheets pressed into the mold slabs, has been developed in the case at hand, for which the cylindrical sample is submitted to heat in the calorimeter cell. The heat flux transferred between the sample and calorimeter detector has been calculated during the cure process, as well as the profiles of temperature and state of cure obtained throughout the mass as a function of the radius. The problem has been solved by using a numerical method with finite differences [11] applied to the cylindrical sample. The kinetic parameters found in previous works [12,13] are considered as constant throughout the total reaction in order to simplify the study.

THEORETICAL

Mathematical treatment of the problem

Several basic assumptions are made for heat transfer process and kinetics of reaction in the sample:

(1) the sample is cylindrical in shape with a circular cross-section of 6 mm diameter;

(2) The flow of heat is radial, the longitudinal heat transfer being neglected;

(3) there is no flow, no molecular diffusion for heat transfer;

(4) the quality of the contact between the sample and calorimeter vessel will be discussed. The effect of the aluminium holder is neglected, because of its high heat transfer;

(5) the parameters of the overall reaction kinetics are assumed to be constant throughout the reaction;

(6) the decrease of free sulfur follows the first-order law with respect to time.

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

$$\left[\rho C \frac{\partial T}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r}\left(r\lambda \frac{\partial T}{\partial r}\right)\right] + \rho \frac{dQ}{dt} \tag{1}$$

The overall rate of cure is given by the simple expression with a constant activation energy

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

where $Q_{r,t}$ is the heat of reaction evolved up to time t on the circumference of radius r.

Initial and boundary conditions obey the above assumptions

$$t = 0 \quad 0 \leqslant r \leqslant R_s \quad T = T_r \quad \text{sample space} \tag{3}$$
$$t > 0 \quad\quad r \geqslant R_s \quad T = T_m \quad \text{oven space}$$
$$\quad\quad 0 \leqslant r < R_s \quad T = T_{r,t} \quad \text{rubber space} \tag{4}$$

Numerical analysis

Because of the internal heat generated from the reaction which is a function of time and space, eqns. (1) and (2) cannot be solved mathematically.

Let the circular cross-section be divided into several circles of radius r, $r + \Delta r$, $r + 2\Delta r$, with Δr the constant radius increment.

On the circumference of radius r at the time $(i + 1)\Delta t$, the temperature after the elapse of the finite incremental time Δt is a function of the temperature at the preceding time $i\Delta t$ on the circumference

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

Another equation must be used for calculating the temperature in the middle of the sample, because eqn. (5) is not applicable for $r = 0$.

$$T_{i+1,0} = \frac{4}{M}(T_{i,\Delta r} + T_{i,0}) + \frac{1}{C} \frac{dQ}{dt}\Delta t \tag{6}$$

On the cylindrical face, the heat balance gives

$$T_{i+1,R_s} = \frac{H}{1+H} T_{i,m} + \frac{1}{1+H} T_{i,R_s} \tag{7}$$

where H is defined by the equation

$$H = \left(\frac{\alpha_m}{\alpha_s}\right)^{1/2} \frac{\lambda_s}{\lambda_m} \tag{8}$$

In both cases, the modulus M is defined as follows

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

The heat flux (HF) between the heat flux detector and cylindrical sample is obtained from the simple equation

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

The heat evolved by the cure reaction during time Δt is calculated with the help of the recurrent relation

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

where $Q_0 = 0$ and

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

EXPERIMENTAL

Sample

The rubber compound was described in a previous paper [10]. The values obtained for the parameters concerned with the kinetics of reaction and heat conductivity through the rubber are shown in Table 1. Throughout the study, these parameters remain constant and non-temperature dependent [14].

Good contact is made between the rubber sample and the holder, as well as between the holder and the calorimeter vessel. The first point is easy to obtain because of the compressibility of rubber. The other point depends on the dimensions of the calorimeter vessel and holder. In any case, we cannot expect a perfect contact and high heat transfer. This problem is responsible for a retardation in the heat flux evolved by the cure reaction, and it will be discussed in detail in another paper.

TABLE 1

Parameters concerning the rubber sample

Heat transfer	$\lambda = 55 \times 10^{-3}$ cal s^{-1} cm^{-1} deg^{-1}; $C = 0.37$ cal g^{-1} deg^{-1}; $\alpha = 10^{-3}$ cm^2 s^{-1}
Cure enthalpy	$Q_\infty = 10$ cal g^{-1}
Kinetic reaction	$n = 1$; $K_0 = 3 \times 10^9$ s^{-1}; $E = 25.400$ cal mol^{-1}
Sample	$R = 0.3$ cm; $T_i = 20°C$; $T_m = 160$–170–$180°C$
Increments	$\Delta r = 0.025$ cm; $\Delta t = 0.125$ s; $H = 1$

Calorimeter

A DSC 111 [15] (Setaram) working under isothermal conditions has been used in this study. Two holders (sample and reference) are simultaneously introduced into the sensitive zone of the calorimeter. The heat flux detector, consisting of thermocouples, connects the vessel to a block so that the temperature of the vessel is always close to that of the block. The heat flux transferred is proportional to the signal emitted.

After curing in the DC vessel, the sample is cooled at room temperature and reheated in the DC vessel under the same conditions in order to obtain the baseline.

RESULTS AND DISCUSSION

Total heat flux–time curve

Figure 1 shows the heat flux–time curve obtained by calculation for the cure of the rubber whose characteristics are described in Table 1. The temperature is 20°C for the sample when dropped into the calorimeter, and 170°C for the calorimeter cell. The largest part of the heat flux–time curve is concerned with the endothermic effect corresponding to the heating of the sample. Thus, one minute or so is necessary for the sample temperature to reach that of the calorimeter. Only a very small exothermic effect due to the cure reaction is obtained for $K_0 = 3 \times 10^9$ s^{-1}, in sharp contrast with the preceding large endothermic effect.

Calculation is done in this paper by taking a value of 1 for the coefficient H defined in eqn. (8). This value is rather small, but it is difficult to get a more precise value for H at the present time. Although the effect of the value given to H is not very important with respect to the heat transfer [11,12] and heat flux–time curve, another study will be necessary for measuring and calculating this coefficient in the case of the sample in the calorimeter cell.

Figure 1 also illustrates the development of heat transfer through the sample during the first minute of the sample in the calorimeter. Very important temperature gradients are developed over the sample radius, especially in the first period of heating.
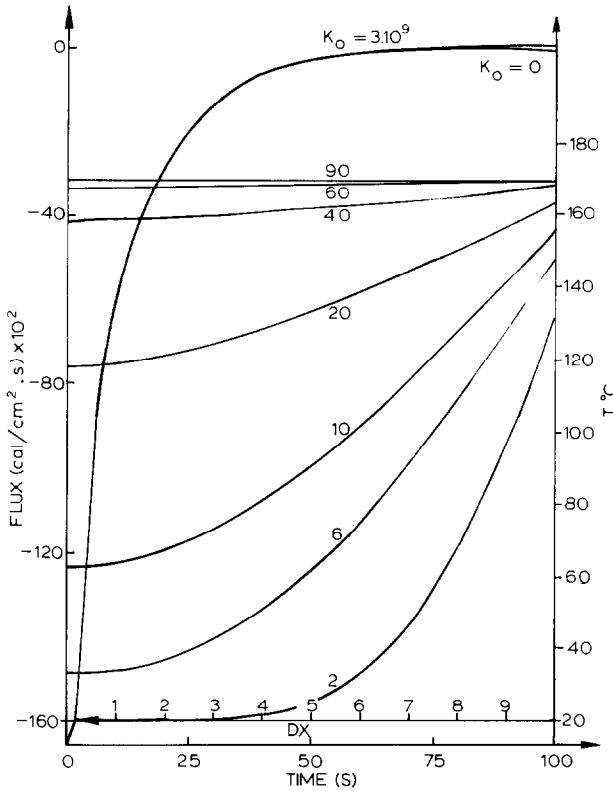
Fig. 1. Heat flux vs. time calculated at 170°C for $K_0 = 3 \times 10^9$ s^{-1} and $K_0 = 0$; $H = 1$. Profiles of temperature at different times (s).
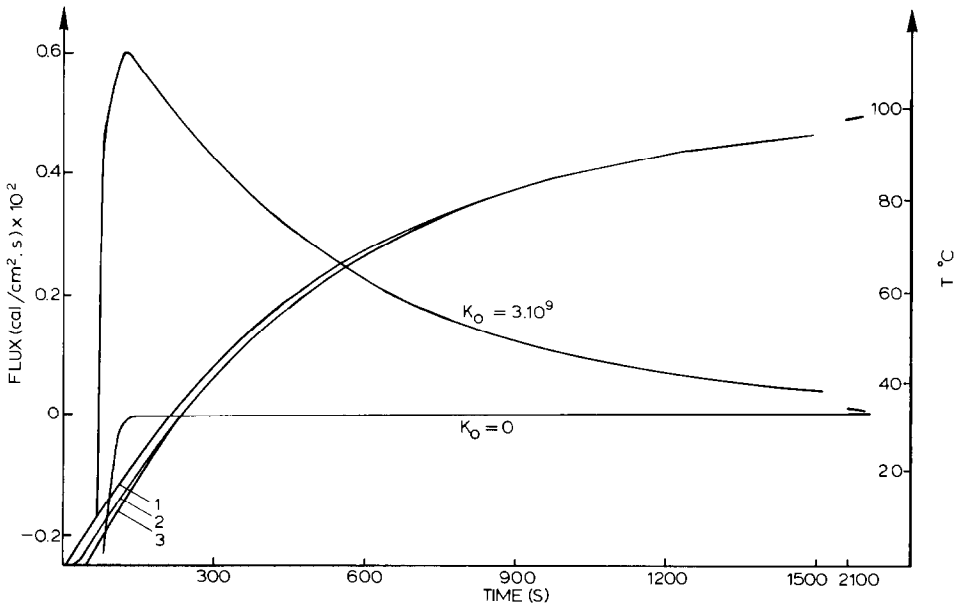

Fig. 2. Heat flux vs. time calculated for heated rubber ($K_0 = 3 \times 10^9$ s^{-1}) at 180°C, and reheated rubber ($K_0 = 0$). $H = 1$. SOC vs. time at different places throughout the sample: (1) $r = R$; (2) $r = R/2$; (3) $r = 0$.

Comparison between heat flux–time curves and profiles of temperature and state of cure

The exothermic part of the heat flux is expressed as a function of time in Fig. 2, as obtained by calculation. Two types of curves are shown, one corresponding to the first cure reaction ($K_0 = 3 \times 10^9/\text{s}^{-1}$), and the other to the reheated sample with no reaction ($K_0 = 0$).

Figure 2 also illustrates the increase in the state of cure obtained at different places in the sample.

The increase in the temperature obtained at the same places in the sample during this period is clearly shown in Fig. 3, as well as the profiles of temperature developed through the sample in Fig. 4.

A comparison between all the results illustrated in Figs. 2–4 is of great interest. We can simultaneously follow the profiles of the heat flux developed through the calorimeter–sample interface, and those of the temperature and state of cure obtained at different places through the sample. An important result is worth seeing, concerning the fact that the maximum of heat flux is measured at about the same time at which the maximum of temperature in the sample is obtained, as can be appreciated from Figs. 3 and 4. This fact will be taken into account for determining the kinetics of cure reaction with the help of the heat flux–time curve (expressing the
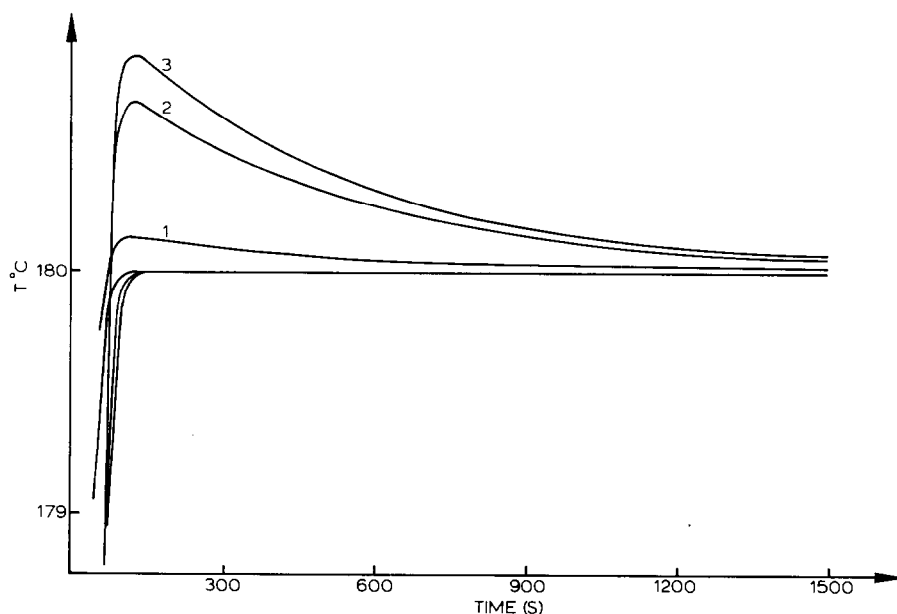

Fig. 3. Temperature vs. time curves at different places for heated rubber ($K_0 = 3 \times 10^9 \text{ s}^{-1}$) at 180°C, and reheated rubber ($K_0 = 0$). $H = 1$. (1) $r = R$; (2) $r = R/2$; (3) $r = 0$.
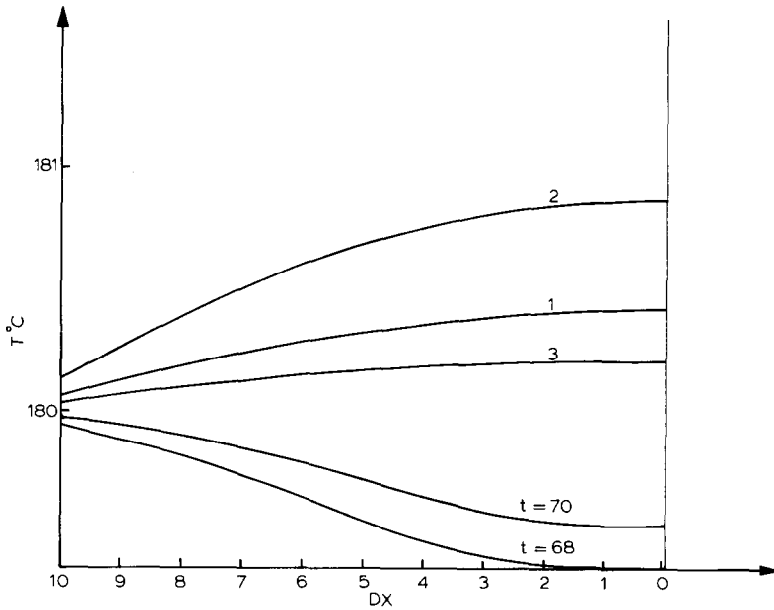
Fig. 4. Profiles of temperature developed through the cross-section of the sample: (1) when heat flux = 1/2 heat flux maximum; (2) when heat flux is maximum.
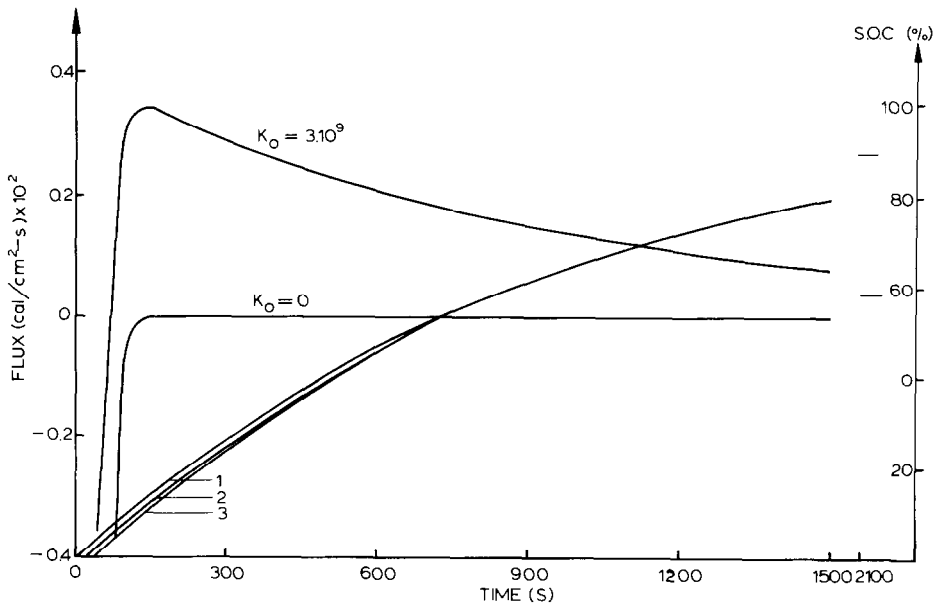

Fig. 5. Heat flux vs. time calculated for heated rubber ($K_0 = 3 \times 10^9$ s^{-1}) at 170°C, and reheated rubber ($K_0 = 0$). $H = 1$. SOC vs. time at different places through the sample: (1) $r = R$; (2) $r = R/2$; (3) $r = 0$.

variation of cure rate with the time), if correct values for the kinetic parameters are wanted.

Effect of calorimeter temperature

The effect of the temperature in the calorimeter on heat flux–time curves can be appreciated by comparing Figs. 2 at 180°C, 5 at 170°C and 6 at 160°C. The profiles of temperature developed through the sample can also be compared in Figs. 3 (180°C), 7 (170°C) and 8 (160°C).

There is a limitation of the temperature range over which experiments can be accomplished with success. On the one hand, too low a temperature for cure studies is limited by the heat flux detector sensitivity, as well as by the time-consuming experiment. On the other hand, the highest temperature provokes a higher sensitivity for heat flux measurements, but it cannot be of any help for studying the induction period of the cure reaction.

All these results are quantitatively expressed in Table 2, where the characteristics of the maximum value of heat flux can be compared: the value of the maximum heat flux (cal cm^{-2} s^{-1}; the value ΔT at which the temperature is raised in excess of that of calorimeter cell, by considering the middle of the sample ($r = 0$) and the position at which $r = R/2$.
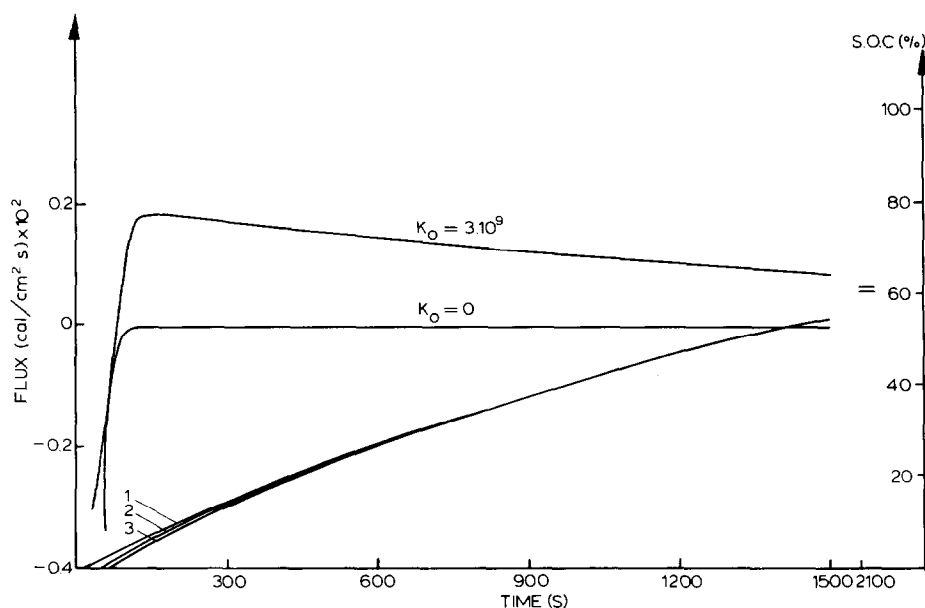

Fig. 6. Heat flux vs. time calculated for heated rubber ($K_0 = 3 \times 10^9$ s^{-1}) and reheated rubber ($K_0 = 0$) at 160°C. $H = 1$. SOC vs. time at different places throughout the sample: (1) $r = R$; (2) $r = R/2$; (3) $r = 0$.
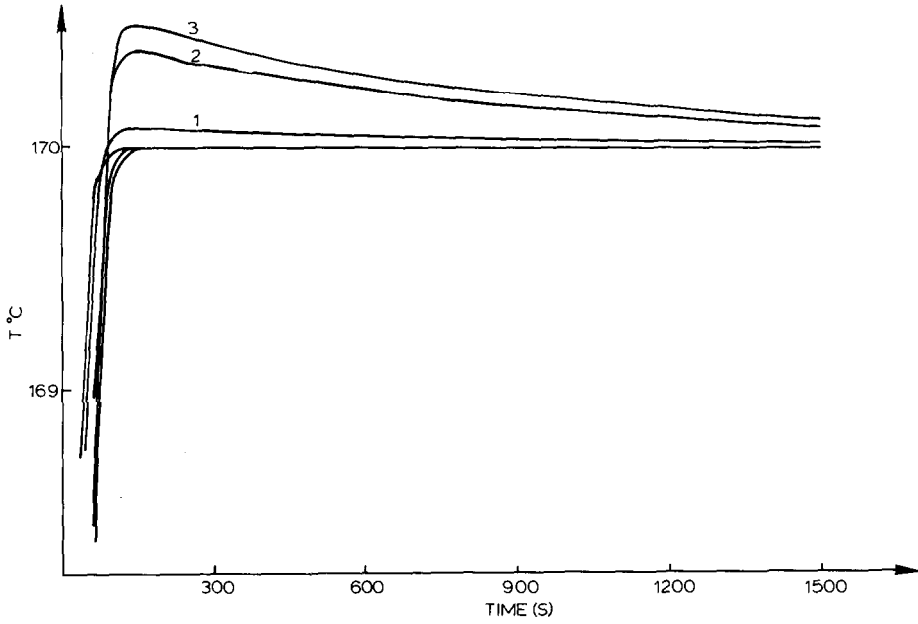
Fig. 7. Temperature vs. time curves at different places for heated rubber at 170°C, and reheated rubber. $H = 1$. (1) $r = R$; (2) $r = R/2$; (3) $r = 0$.
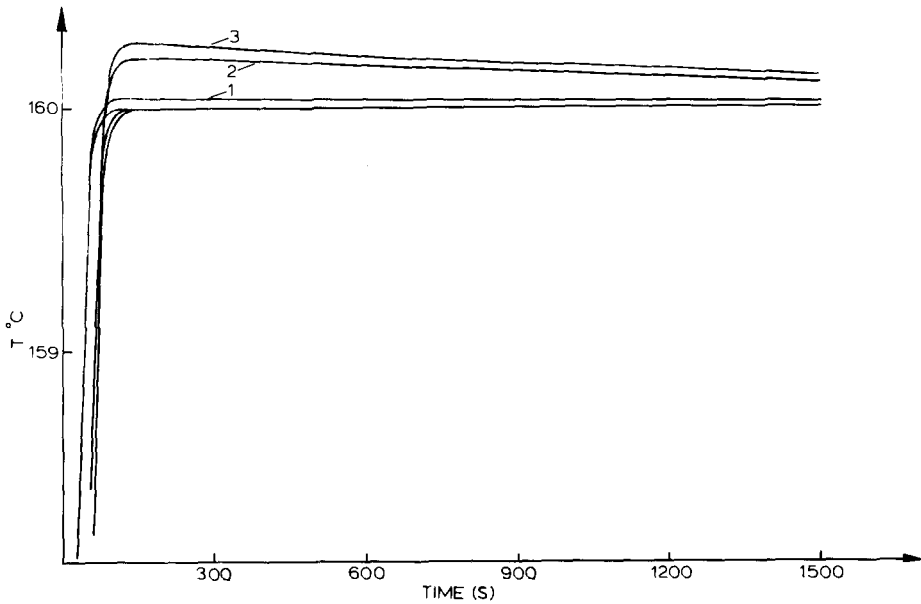

Fig. 8. Temperature vs. time curves at different places for heated rubber and reheated rubber at 160°C. $H = 1$. (1) $r = R$; (2) $r = R/2$; (3) $r = 0$.

TABLE 2

Characteristics of maximum of heat flux

Calorimeter T (°C)	160	170	180
Heat flux max. (cal cm^{-2} s^{-1})	0.18	0.34	0.60
ΔT in sample middle (°C)	0.26	0.50	0.88
ΔT for $r = R/2$	0.20	0.39	0.69

CONCLUSIONS

This paper has been devoted to the study of the heat flux obtained in calorimeter detector of rather large size (100–200 mg), by considering the cure of rubber with a low enthalpy (10 cal g^{-1}).

Because of low heat transfer through the rubber, high gradients of temperature and, consequently, of state of cure are developed throughout the cross-section of the cylindrical sample. The method described here has allowed one to calculate the profiles of temperature and state of cure developed through the rubber at different times, as well as the heat flux evolved through the sample–calorimeter detector interface. This advanced method uses kinetic data for the heat produced by the cure reaction and chemical engineering laws on heat transfer by conduction, as well as numerical analysis and computerization. The heat flux–time curves calculated are in good agreement with the experimental curves determined under the same conditions.

With the help of this simultaneously obtained information, we can get a good " view" of the inside of the sample itself while the reaction is progressing. Therefore, an accurate and precise method for determining the parameters of the kinetic of reaction will have to take all these results into account, by considering that a reaction cannot work under isothermal conditions. This is the first step in taking thermoanalytical methods to a higher degree of refinement.

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 of cross-section of cylindrical sample
r	radius of cross-section circumference
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
α thermal diffusivity
n order of overall cure reaction
K_0 rate constant of reaction
E activation energy

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