

ENHANCED STUDY OF THE METHOD OF COUPLING DSC AND DC TECHNIQUES FOR RUBBER CURE IN 200-mg SAMPLES

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ABSTRACT

A method coupling differential scanning calorimetry and differential calorimetry according to a two-step process is studied for the case of rubber cure. At the beginning a temperature programme is used for the calorimeter, followed by heating under isothermal conditions. This method is investigated by using a model which takes into account the kinetics of heat evolved by the overall cure reaction, and the heat transferred by conduction through the calorimeter-sample interface and a cylindrical sample of 6 mm diameter. More detailed information is thus obtained. Not only are the heat flux-time curves predicted by calculation in good agreement with the experimental ones, but also the following curves are calculated as a function of time: the profiles of temperature and state of cure developed through the sample. These results lay the foundations for another new method allowing workers to obtain kinetic parameters in spite of these temperature variations.

INTRODUCTION

Most of the techniques developed to characterise the cure process for rubbers and the nature of vulcanizate are time-consuming and tedious [1]. On the contrary, differential scanning calorimetry (DSC) and differential calorimetry (DC) are of interest. In both DSC and DC techniques, the enthalpy changes accompanying a physical or chemical 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 with a constant heating rate (DSC), or as a function of time, the calorimeter being held at constant temperature (DC).

Of course, these two techniques exhibit some advantages and drawbacks. It seems to be easier to study the kinetics of reaction by working under isothermal conditions. A well-known disadvantage of DC techniques is the

lack of information at the beginning of the process, just after the sample has been dropped into the calorimeter. In fact, during this time (ranging from 20 to 60 s, depending on the size of the sample and calorimeter) high gradients of temperature are developed through the sample and a significant endothermic heat flux is emitted from the calorimeter to the sample, giving no useful information.

Moreover, dispersion problems do arise on occasion and are generally observed by lack of reproducibility in both DSC and DC curves. The question which always arises is how representative is a 200-mg sample taken from a large batch (25 kg of rubber on industrial scale, 100 g when using laboratory equipment) of the homogeneity of the batch. Occasions have arisen when sulfur is poorly dispersed either because of poor milling practices or because of too large particles of sulfur failing to be broken down [2]. A larger size (100–200 mg) would perhaps be of help to reduce the above effect due to the lack of homogeneity, but high gradients of temperature and state of cure are developed through the sample during the cure cycle.

Vulcanisation of elastomers is a process whereby chemical cross-links are introduced between the elastomer chains, resulting in the formation of a three-dimensional network. Overall, the chemistry accompanying sulfur vulcanisation is extremely complex, and detailed kinetic analysis of the enthalpy profile has not been feasible up to now for the complex reactions present in the sample. However, the heat evolved by the overall cure reaction can be described at times by a single reaction with a constant activation energy [3,4].

In the present work, the information that can be obtained from DC profiles on the curing process is considered. The method used successively combines DSC and DC techniques according to a two-step process. After the sample is put into the calorimeter cell, the temperature of the calorimeter is programmed with a constant heating rate from room temperature to a constant value, and it is followed by heating under isothermal conditions. Thus, lower gradients of temperature and state of cure can be expected, in contrast to those obtained with the DC approach. The purpose of this work being to afford a further insight into the cure operation obtained with this technique, some calculations are completed at the same time: heat flux evolved by the cure reaction, profiles of temperature generated through the sample and the resulting profiles of state of cure, all these results being obtained as a function of time.

In previous works, it was pointed out that these profiles of temperature and state of cure can be calculated while they are developed through rubber sheets [4,5] or cubic samples [6]. The model used in this paper is modified in order to be applied to a cylindrical sample, in which radial heat is conducted by convection through the circular cross-section of the sample and the calorimeter–sample interface. It also takes into account the heat evolved by the cure reaction, whose kinetics were previously determined [3,4].

THEORETICAL

Assumptions

In the present study the following assumptions have been made:

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

(ii) the heat transfer is only radial, and heat conduction through the rubber is considered;

(iii) the heat transfer through the calorimeter-sample interface is estimated, by taking into account the quality of the contact between the above two materials;

(iv) the kinetics of the overall reaction of cure follow a single reaction with a constant activation energy;

(v) the parameters characterizing heat transfer through the rubber are not temperature-dependent.

Equations in non-steady state

As a result of these assumptions, the radial heat conduction is governed through the circular cross-section by the following equations

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

In this equation, the increase in the temperature (on the left) is equal to the sum of two contributing terms: that concerned with heat conduction, and that with heat evolved from the cure reaction.

The rate of the rubber cure is given by a classical one-order reaction

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

in which Q_∞ is the total cure enthalpy, and $Q(r, t)$ the heat of cure evolved up to time t at position r in the cross-section.

As the temperature of the calorimeter is varied according to the following program: linear increase in temperature from room temperature to a constant value, followed by heating under isothermal conditions, the equation is in this case

$$T_t = 20 + bt \quad (3)$$

where b is the heating rate.

The following two equations describe the initial and boundary conditions in the cylindrical sample dropped into the calorimeter.

$$t = 0 \quad 0 \leq r \leq R_s \quad T = T_r \quad \text{rubber space} \quad (4)$$

$$t > 0 \quad r \geq R_s \quad T = T_m \quad \text{oven space} \quad (5)$$

$$0 \leq r < R_s \quad T = T_{r,t} \quad \text{rubber space}$$

No solution of the present problem can be deduced in a mathematical

way.

Numerical treatment

A numerical analysis is needed to resolve this problem. An explicit method with finite differences is chosen in our case, because of its interest for microcomputers.

After dividing the cross-section of the sample into successive circles with the following values for the radius: $r - \Delta r$, r , $r + \Delta r$, (Δr being a constant increment) the heat balance for the ring between $r - \Delta r/2$ and $r + \Delta r/2$ gives

$$T_{i+1,r} = \frac{1}{M} [T_{i,r+\Delta r} + (M-2)T_{i,r} + T_{i,r-\Delta r}] + \frac{\Delta r}{2Mr} [T_{i,r+\Delta r} - T_{i,r-\Delta r}] + \frac{1}{C} \frac{dQ}{dt} \Delta t \quad (6)$$

during the increment of time Δt .

The increment of time is related to the increment of space in the dimensionless modulus.

$$M = \frac{(\Delta r)^2}{\Delta t} \frac{1}{\alpha_s} \quad (7)$$

where α_s is the heat diffusivity of the sample.

Equation (8) is used for the middle of the cross-section where $r = 0$, instead of eqn. (6).

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

in which $T_{i+1,0}$ is the temperature in the middle of the cross-section at time $(i+1)\Delta t$.

Another equation must be used for describing the heat transfer through the calorimeter-sample interface, because of the discontinuity between these two different kinds of materials. The coefficient H is expressed as a function of heat diffusivities and thermal conductivities of the calorimeter oven and sample.

$$H = \left(\frac{\alpha_m}{\alpha_s} \right)^{1/2} \frac{\lambda_s}{\lambda_m} \quad (9)$$

The temperature on the sample surface at time $(i+1)\Delta t$ is then given by

$$T_{i+1,R_s} = \frac{1}{1+H} T_{i,m} + \frac{1}{1+H} T_{i,R_s} \quad (10)$$

where $T_{i,m}$ is the temperature of the calorimeter following eqn. (3).

In this work, as in other earlier papers concerned with the cure of rubber [3-5], the state of cure is described as the ratio of the heat evolved up to time t to the total heat of cure. The heat of cure evolved up to time t is calculated

by slightly modifying eqn. (2).

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

While

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

Heat flux transferred from the calorimeter oven to the sample has to be determined in this work. It is easily obtained by using eqn. (13).

$$\text{Heat flux} = \lambda_s \frac{T_{R_s} - T_{R_s - \Delta r}}{\Delta r} \quad (13)$$

As it is conventional to suppose that heat is positive when received by the system studied, heat flux is exothermic when the temperature of the sample is higher than that of the calorimeter oven.

EXPERIMENTAL

Method

Thermal investigations are carried out with a DSC (Setaram) working in scanning mode for the first step of heating and under isothermal conditions for the second step.

The stainless-steel holder is cylindrical in shape and the circular cross-section has a diameter of 6 mm. The holder face is as close as possible to that of the calorimeter block, but the contact is not perfect, as in all other apparatus. As the block is cylindrical, it surrounds the holder pretty well and only a negligible part of the heat flux is lost.

Operation conditions are as follows: the temperature is programmed from 20°C to the constant temperature chosen, the rate of heating being 5°C min⁻¹. The values chosen for constant temperature range from 160 to 180°C.

After curing in the DSC vessel, the sample is cooled at 20°C and reheated in the calorimeter under the same conditions as above, giving the baseline for heat flux–times curves.

Materials

As described in a previous paper [3], a rubber powder–sulfur mixture is used as the sample. 2% sulfur as vulcanizing agent is preliminarily mixed with the 50–250 μm grain-size rubber. The kinetic parameters for the cure reaction were determined previously, and they are shown in Table 1.

TABLE 1

Kinetic parameters of cure reaction

Cure enthalpy, $Q = 10 \text{ cal g}^{-1}$;
 $n = 1$; $K = 3 \times 10^9 \text{ s}^{-1}$; $E = 25400 \text{ cal mol}^{-1}$;
 Sample = 150 mg; $R_s = 0.3 \text{ cm}$;
 Heat transfer = $10^{-3} \text{ cm}^2 \text{ s}^{-1} C = 0.37 \text{ cal g}^{-1} \text{ }^\circ\text{C}^{-1}$

Calculation

Heat flux is calculated, as well as the temperatures and state of cure developed through the cross-section in the sample, by using the conditions for numerical analysis given in Table 2.

In contrast to the method of Schmidt [7] in which the value of 2 is employed to obtain simple equations, we have always preferred to use a higher value for M preventing the temperature from oscillating alternately above and below that of the analytical solution [6].

RESULTS

Heat flux-time curves and profiles of temperature and state of cure

A chemical reaction occurs during the heating period in the case at hand, and heat transfer plays a particularly important role, because the rate of the reaction increases rapidly with small increases in temperature. For instance, an increase in temperature of the mold of about $7\text{--}10^\circ\text{C}$ is responsible for doubling the rate of cure. Although the enthalpy of cure reaction is not very important (about 4–5 calories per gram of mixture for 1% sulfur), the increase in temperature may become significant because of the very low heat conductivity of rubber.

In order to obtain insight into the problem of rubber cure, it is of interest to gain a deep knowledge of the whole process while using DSC or DC techniques for determining the kinetics of reaction. This is the reason why we have determined by calculation not only the heat flux-time curves obtained during the DC process described above, but also the profiles of

TABLE 2

Parameters for calculation

Radius, $R_1 = 0.25 \text{ cm}$; number of cylindrical slide = 10;
 Increments, $\Delta r = 0.025 \text{ cm}$; $\Delta t = 0.2 \text{ s}$; $M = 3.12$;
 $H = 1$

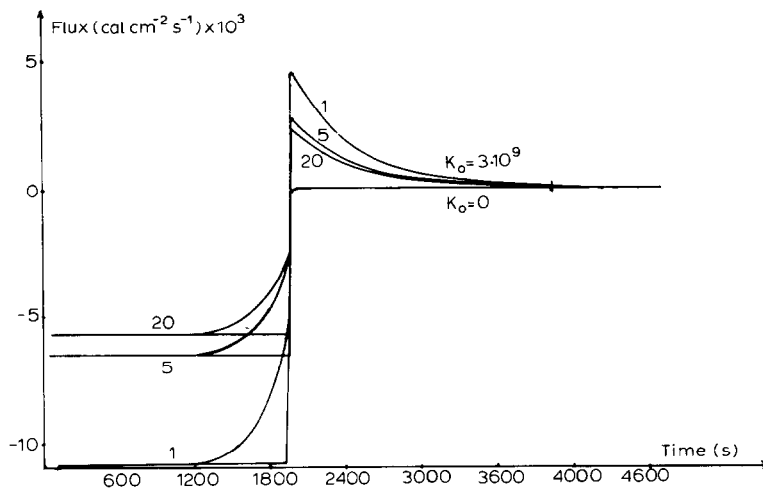


Fig. 1. Heat flux-time curves for different values of H , while the temperature of the calorimeter is 180°C . $H = 1, 5, 20$; $K_0 = 3 \times 10^9 \text{ s}^{-1}$, $K_0 = 0$.

temperature and state of cure developed through the sample at the same time.

Figure 1 represents the heat flux evolved through the sample-calorimeter interface as a function of time. Heat flux is of interest because of its proportionality to the rate of reaction. These curves are calculated by using different values for the coefficient H shown in eqn. (9). The value of 1 chosen for H corresponds to the case of perfect rubber-rubber contact, and 20 is the value obtained for rubber-steel contact. The effect of the quality of the contact between the sample and the calorimeter is particularly set out in the experimental. These results correlate well with experimental curves in shape, especially in the exothermic part where the cure reaction takes place. A slight difference may be observed during the temperature-programmed period, because of the variation in the heat capacity of rubber with temperature. The baseline is obtained by taking 0 for the rate constant, K_0 , in the model described above.

As an extension of this study using our model, we have also obtained the profiles of temperature developed against time, at different places through the circular cross-section of the sample. Figure 2 shows that all temperature-time curves pass through a maximum, this maximum value of the temperature being found when the heat flux has the highest value. Significant gradients of temperature can be appreciated through the rubber sample during cure, and this interesting fact will surely generate great difficulties to be coped with in studying the kinetics of reaction more precisely.

An additional investigation is achieved, concerned with the state of cure (SOC). The state of cure, as calculated at different places in the sample, is

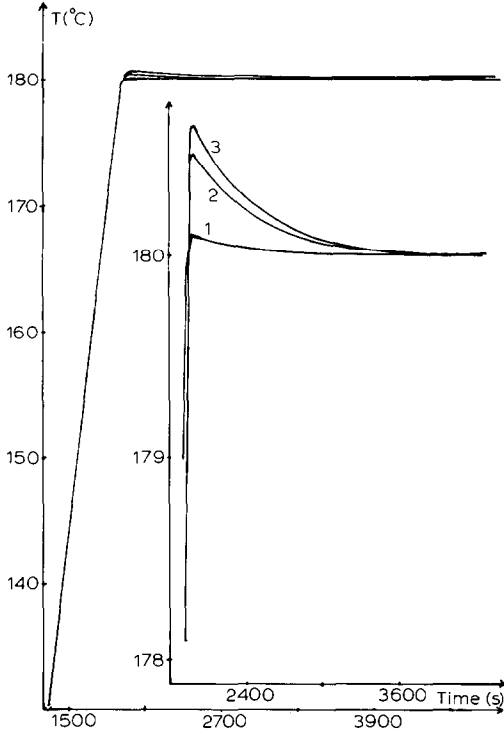


Fig. 2. Temperature vs. time in different places of the sample: (1) sample face; (2) $r = R/2$; (3) middle; $H = 1$; temperature of calorimeter = 180°C.

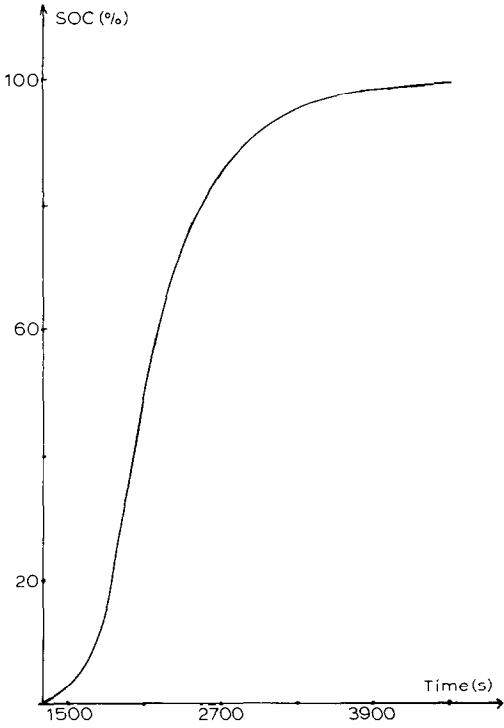


Fig. 3. SOC vs. time in different places: $H = 1$; temperature of calorimeter = 180°C.

shown in Fig. 3. This result demonstrates that no significant profile of the SOC can be appreciated through the sample. The increase in the state of cure exhibits the well-known inverted-S shaped curves.

In continuation of our previous studies on thick and thin rubber sheets [3–6], the results concerning the cure process obtained in the sample with the DSC technique are reported below. The purpose of this work is attained, giving new and complementary information: the rate of reaction as a function of time, as well as the profile of temperature and state of cure shown at the same time. In spite of this complication, we think that large samples of about 200 mg are of interest, being representative of what happens on an industrial scale.

Effect of the temperature of the calorimeter

As the method studied in this paper combines DSC and DC techniques, the parameter of interest is the constant temperature applied at the end of the programme. Three different values are chosen for this temperature, ranging from 160 to 180°C.

Effect of the applied temperature on heat flux

Heat flux–time curves obtained by calculation are shown in Figs. 1 (180°C), 4 (170°C) and 5 (160°C) with the same coefficient H characterising the quality of contact between the sample and the calorimeter vessel.

The following facts are worth noting.

(1) The calculated curves are in good agreement with the corresponding experimental ones, except a small variation in the baseline obtained during

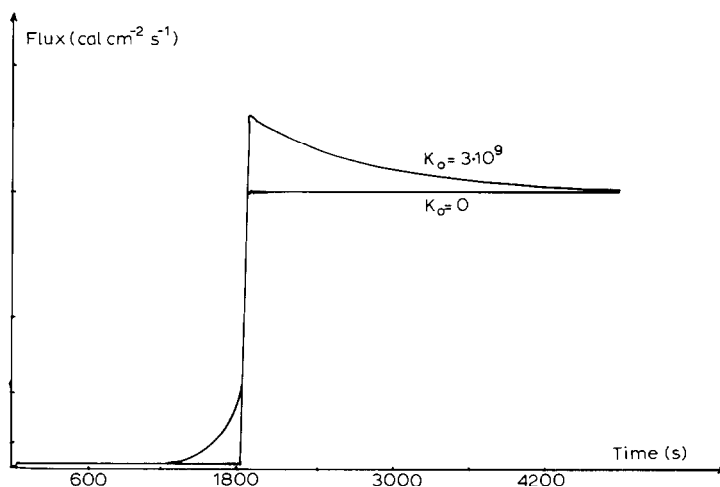


Fig. 4. Heat flux–time curves for $H = 1$; temperature of calorimeter = 170°C.

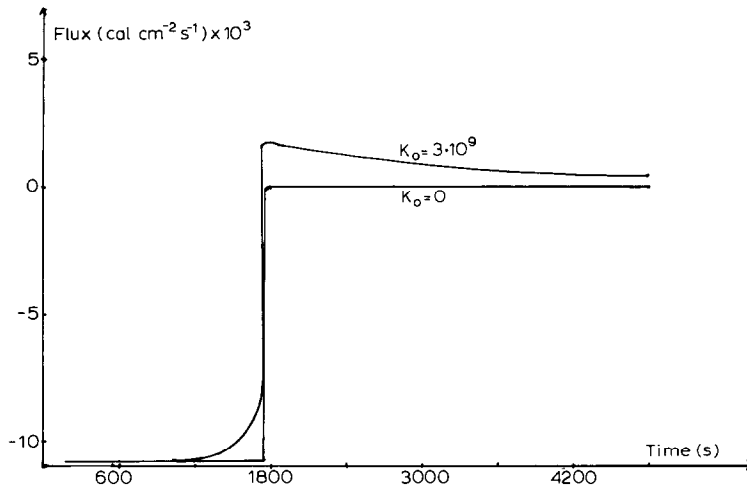


Fig. 5. Heat flux-time curves for $H=1$; temperature of calorimeter = 160°C .

the programming step. This last divergence is due to the fact that our calculation is performed without taking into account any change in heat capacity of the materials.

(2) Heat flux and reaction start to occur at the same time (around 1200 s) and at the same temperature (120°C). Therefore, a part of the reaction has already started during the first step of the programme, before reaching the constant temperature. This part of the cure reaction can be clearly appreciated in the above three figures, and might be studied by using available methods. Of course, the lower the constant applied temperature, the smaller this part of the reaction will be with regard to the whole reaction.

(3) For a low applied temperature, the heat flux and rate of enthalpy change are very small, and it takes a long time for the reaction to proceed to completion. Moreover, the sensitivity is decreased in this case.

Profiles of temperature through the sample

Temperature is determined as a function of time in three positions in the sample as shown above for the three applied temperatures: Fig. 6 at 170°C ; Fig. 7 at 160°C ; Fig. 2 at 180°C . The profiles of temperature developed through the sample can be appreciated from these curves. Three results can be distinguished:

- (1) The temperature is highest in the middle of the sample;
- (2) The maximum value for these temperatures is obtained when the rate of cure has reached its highest value;
- (3) The higher the applied temperature in the calorimeter, the higher the values maximum temperature reached in the sample. Quantitative results are given in Table 3, where the difference between the maximum temperature in sample and that of the calorimeter is determined as a function of the

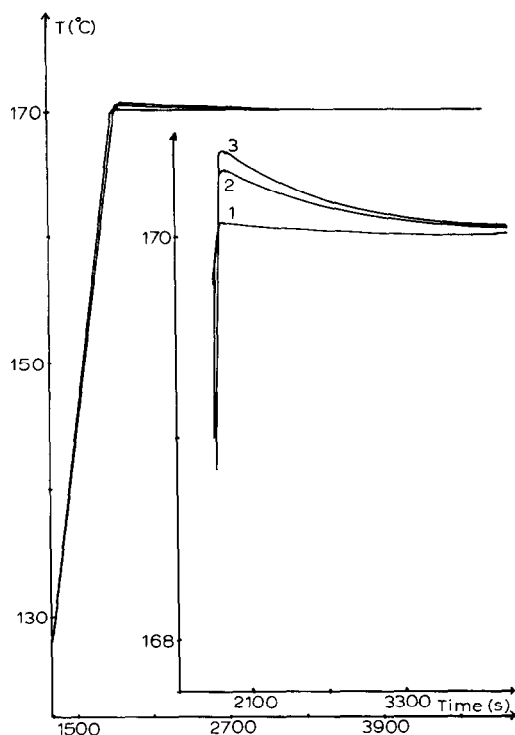


Fig. 6. Temperature vs. time in different places of the sample: (1) sample face; (2) $r = R/2$; (3) middle; $H = 1$; temperature of calorimeter = 170°C .

position in the sample and the value of the applied temperature.

Effect of applied temperature on the state of cure

Figure 8 shows the increase in the state of cure as a function of time, for the three values of the applied temperature, while the coefficient H is 1.

The value of the state of cure obtained at the end of the temperature programme can be seen in the three cases.

There is some difficulty in appreciating the time necessary for the cure reaction to reach completion. In fact, only values of 90 or 95% for the state of cure are of interest.

TABLE 3

Temperature in excess versus applied temperature

Applied T ($^{\circ}\text{C}$)	160	170	180
Middle	0.25	0.42	0.65
$r = R/2$	0.19	0.32	0.40

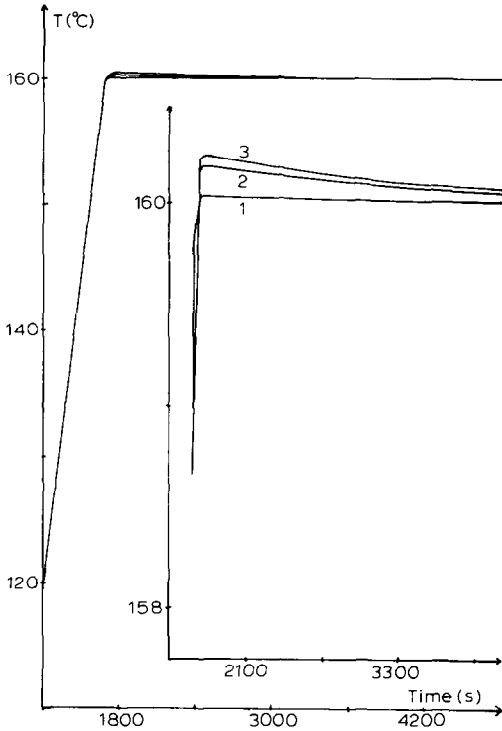


Fig. 7. Temperature vs. time in different places of the sample; (1) sample face; (2) $r = R/2$; (3) middle.

Quality of the contact between sample and calorimeter

The value of the coefficient H has been defined to quantify the quality of contact at the sample-calorimeter interface.

The effect of the value given to H on the rate of cure can be appreciated in Fig. 1 while the applied temperature is 180°C . The higher the quality of contact, the higher the sensitivity for heat flux. Fortunately for this technique, however, these curves obtained with different values of H are similar in shape, and there is a constant ratio of similarity at any point taken along the curves, as shown in Table 4.

TABLE 4
Effect of H on the ratio of similarity

H	1	5	20
Heat flux max.	45	27	23
2400 s	20	12	10
2700 s	10	6	5

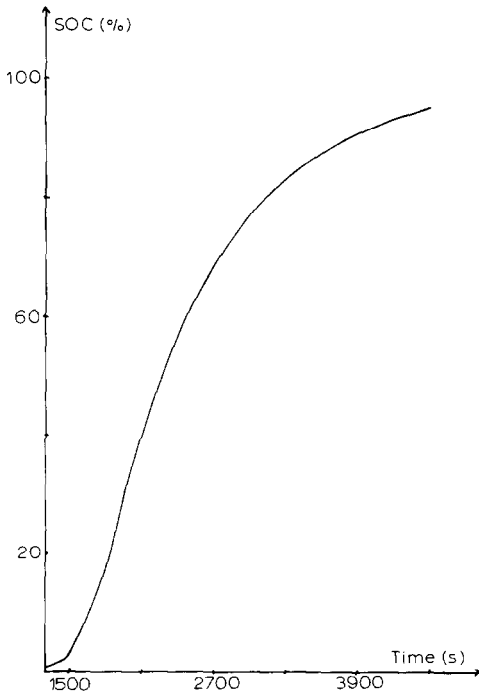


Fig. 8. Effect of temperature of calorimeter on SOC-time curves for $H = 1$.

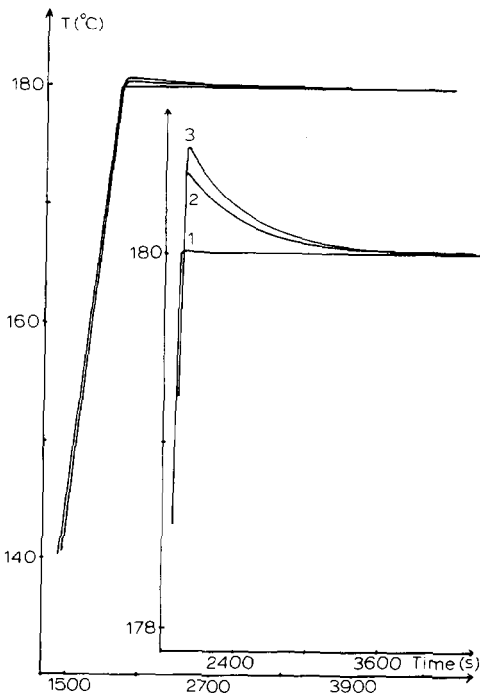


Fig. 9. Temperature vs. time in different places of the sample: (1) sample face; (2) $r = R/2$; (3) middle; $H = 20$; temperature of calorimeter = 180°C .

The effect of the quality of contact on the profiles of temperature expanded through the sample can be appreciated by comparing the curves drawn in Figs. 2 and 9. They are obtained for the same value of the applied temperature (180°C), the former with $H = 1$ and the latter with $H = 20$. The temperatures are about the same throughout the sample, and the single, slight difference can only be seen on the sample face.

In much the same way as for the temperature, the effect of the quality of contact on the state of cure is negligible.

CONCLUSION

Attention has been given in this paper to focus on answering the many remaining questions regarding the DC technique when the reaction studied takes place with a resulting heat flux measured in the calorimeter, and to discover if there are any profiles of temperature growing throughout the sample.

Such a search for this understanding has produced an answer. It has been feasible to calculate simultaneously the heat flux transferred through the calorimeter-sample interface, as well as the profiles of temperature and state of cure developed through a rather large cylindrical sample. To cope with the difficulty, we have looked at the problem of a model described in recently published papers, and have explored its feasibility. We have set much importance upon the actual temperature within the sample, slightly devaluating the value usually measured for heat flux in the DC technique. A new factor has been found to be of importance concerned with the quality of contact at the sample-calorimeter interface.

The practical application of these results for determining more accurate parameters for the kinetics of reaction has yet to be made. However, this work has laid the way to this final result.

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