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COMPARATIVE STUDY OF A REACTION OF LOW ENTHALPY (RUBBER CURE) BY DC AND DSC

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ABSTRACT

The two techniques of calorimetry, the first using isothermal conditions (DC) and the second using a scanning mode (DSC) are compared by considering a reaction of low enthalpy (5 cal g^{-1}) (rubber cure). It is necessary to use a large sample (150 mg), because of the difficulty of dispersing the ingredients in the rubber. The model used takes into account not only the kinetics of reaction of the cure, but also the heat transferred by conduction through the rubber. The kinetics of the heat evolved from the cure reactions is determined by DSC using a low heating rate when the effect of heat transfer may be considered negligible. Significant disadvantages of the DC technique are discussed. Because of the time required for the calorimeter to establish thermal equilibrium, the first part of the reaction with the induction period has not been studied and a considerable part of the heat of reaction of the cure is lost. Also very high gradations of temperature occur through the sample, causing the development of an inhomogeneous process. These disadvantages are shown to be less important in the DSC technique.

INTRODUCTION

In this paper a new approach to making a comparative study of calorimetry using isothermal conditions (DC), and differential scanning calorimetry (DSC) is explored. In both techniques, the enthalpy changes accompanying a physical or chemical event in the sample are monitored, and the profile of the rate of enthalpy change is obtained either as a function of temperature as the sample is heated at a known linear rate (DSC), or as a function of time when the calorimeter is held at constant temperature (DC).

The small sample size usually used in calorimetry necessitates that all ingredients in the sample are well dispersed. Dispersion problems do arise on occasion and are generally identified by lack of reproducibility in the heat flux–time curves. The question which always arises is whether a 1–10 mg sample taken from a 1–5 kg batch is representative of the homogeneity of the batch. In the case of rubber, sulfur can be poorly dispersed, either because of poor milling practice or because large particles of sulfur fail to be

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broken down. A 1–10 mg sample can be virtually all sulfur [1]. In the same way, a slight variation in the composition of the binary system of epoxy resin has a significant effect on the properties of the final material [2]. For studies of complex mixtures, it is more desirable to use a larger sample of about 100–200 mg than to undertake repetitive experiments with small samples.

However, although using a large sample in calorimetry gives results more representative of the composition of the material studied and more reproducible experiments, some factors must be taken into account [3]. Heat transfer is generally the first and the most important step in industrial processes, as has been shown in rubber cure [4,5] and epoxide reticulation [6]. Because of the low thermal conductivity of the rubber or resin, high gradients of temperature grow within the mass when the material (initially at room temperature) is put in a heated mold, and these are responsible for considerable heterogeneity in the sample with respect to the state of cure [4,5,7] or mechanical properties [8–10]. This uneven heat transfer also appears in calorimetry, and can be a source of error: (i) the applied temperature is not the true temperature during the cure because of local heating originating from exothermic reactions and of low heat conductivity of the material [4–13]; (ii) high temperature gradients are developed through the sample, making the kinetic study of reactions difficult, especially in DC experiments or in DSC measurements using high heating rates [11–13]. However, these gradients become very important when the enthalpy of the reaction is higher e.g. epoxy resin [14–16].

For both DC and DSC techniques, the process of cure is studied either by experiment and calculation with the help of a model. Although experiments are useful especially in testing the validity of the model and in providing information on the kinetic parameters, the model is capable of giving more information. Our models previously described [11–16] are able to give information on the heat flux emitted through the sample surface, in the same way as in experiments and the profiles of temperature and state of cure developed through the sample. Based on a numerical method with finite differences, these models take into account not only the kinetics of reaction but also the heat transferred through the material by conduction and through the oven–sample interface.

THEORETICAL

Assumptions

Some classical assumptions are made in order to clarify the problem.

(i) Radial heat conduction is considered through the circular cross-section of cylindrical samples, the length of these cylinders being larger than the

TABLE 1

Parameters characterizing the compound

Cure enthalpy 5 cal g^{-1}
Kinetic: $n = 1$; $K_0 = 3 \times 10^9$ s^{-1}; $E = 25400$ cal mol^{-1}
Sample: 150 mg; $R_s = 0.25$ cm
Heat transfer: $\lambda = 9.9 \times 10^{-4}$ cal cm^{-1} s^{-1} deg^{-1}; $\rho = 1.1$ g cm^{-3}; $C = 0.49$ cal g^{-1} deg^{-1}; $\alpha = 1.85 \times 10^{-3}$ cm^2 s^{-1}

diameter, and because of the position of the heat flux captors in the calorimeter.

(ii) The thermal properties of the rubber, as well as the other properties shown in Table 1, are constant during the reaction and heating period.

(iii) The reaction of the cure of rubber samples is expressed by the heat evolved from this reaction. The state of cure (SOC) at time t is thus defined by the heat evolved from the reaction up to time t as a fraction of the total heat evolved.

(iv) The temperature of the holder is the same as that of the calorimeter. The contact between the rubber and the sample is assumed to be perfect.

Mathematical treatment

The classical equation for radial heat conduction is

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

where the contributions of the conduction heat and reaction heat are shown.

In the DC technique, the temperature of the oven in the calorimeter is considered as constant. In the DSC technique, the oven is heated at a constant rate

$$\frac{\partial T}{\partial t} = \text{constant} \tag{2}$$

The initial and boundary conditions are

$$t = 0 \quad 0 < r < R_s \quad T = T_0 \quad \text{sample} \tag{3}$$

$$t > 0 \quad r > R_s \quad T = T_m \quad \text{calorimeter} \tag{4}$$

$$0 < r < R_s \quad T = T_{i,r} \quad \text{sample}$$

The heat evolved from the cure reaction is expressed by eqn. (5) which was found to give interesting results [17]

$$\left(\frac{1}{Q_\infty}\right)\left(\frac{dQ}{dt}\right) = k_0\left(1 - \frac{Qt}{Q_\infty}\right)^n\left(\exp - \frac{E}{RT}\right) \tag{5}$$

Numerical analysis

As no analytical solution can be found for eqn. (1), essentially because of the presence of the internal heat generated by the reaction, the problem is solved by a numerical method with finite differences.

By considering the following circles of radius r, $r+\Delta r$, $r+2\Delta r$, etc., taken through the circular cross-section of the sample, the heat balance is easily determined in the ring between the circles $r+\Delta r/2$ and $r-\Delta r/2$, and the temperature within this ring after time Δt can be obtained from the temperature at the preceding time in the same ring and the two adjacent rings.

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

A particular equation must be used for the middle of the cross-section of the sample

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

In eqns. (6) and (7), M is a dimensionless number expressed as a function of the increment of space Δr and time Δt

$$M=\frac{(\Delta r)^2}{\Delta t}\left(\frac{1}{\alpha}\right) \qquad (8)$$

The heat flux transferred through the calorimeter–sample interface is obtained as follows

$$\mathrm{HF}=\lambda(T_R-T_{R-\Delta r}/\Delta r) \qquad (9)$$

The heat evolved from the cure reaction is calculated with the help of the recurrent relation, when the order n is 1

$$\left(\frac{\mathrm{d}Q}{\mathrm{d}t}\right)_{i+1}\Delta t=Q_{i+1}-Q_i=k_0(Q_\infty-Q_i)\exp-\frac{E}{RT} \qquad (10)$$

where

$$Q_i=\sum_{i=0}^{i}\left(\frac{\mathrm{d}Q}{\mathrm{d}t}\right)\Delta t \text{ and } Q_0=0 \qquad (11)$$

EXPERIMENTAL

Technique and apparatus

A heat-flux calorimeter DSC 111 (SETARAM, Lyon, France) with a temperature programming facility was used. It can be used either under isothermal conditions or in a scanning mode with a constant heating rate [13].

A large sample (150 mg for rubber) was used to solve the problem of dispersion of sulfur in the rubber compound. The sample was encapsulated in a cylindrical steel holder of diameter 5 mm. It was imperative that good contact was made between the rubber material and the holder, and the rubber was forced into the holder. The internal diameter of the calorimeter block was 5.1 mm, allowing good contact between the calorimeter and the holder as shown previously [13].

The calorimeter was coupled with a microcomputer (HP 86-Hewlett Packard), and the heat flux was recorded either as a function of time (DC) or as a function of temperature (DSC).

Materials

A sulfur–rubber compound was used, the main characteristic of which was the total enthalpy of cure of 5 cal g^{-1} which depends on the percentage of sulfur [18,19].

The kinetic parameters for the heat evolved from the total cure reaction have been determined previously by calorimetry using a scanning mode with a low heating rate. They are shown in Table 1, together with the parameters of the heat transfer.

Calculation

The model is used for calculating the heat flux, and the profiles of temperature and state of cure developed through the sample at various times. The parameters used for numerical analysis are shown in Table 2. It is imperative that the number *M* is higher than 3.

RESULTS

Results are expressed in the form of the heat flux emitted through the calorimeter–sample interface and in the form of profiles of temperature and state of cure expanded within the sample.

TABLE 2

Parameters for calculation

Radius = 0.25 cm	Number of circles = 10	
$\Delta r = 0.025$ cm	$\Delta t = 0.05$ s	$M = 6.76$

Calorimetry working under isothermal conditions (DC)

In this technique, the calorimeter is stabilized at the desired temperature, the sample previously at room temperature is introduced and time base recording is started. The enthalpy changes accompanying the chemical event taking place in the sample are monitored, and the result is the profile of the rate of enthalpy change as a function of time. The enthalpy associated with the overall exotherm is determined by measuring the area under the exotherm after selection of the reference baseline. This reference baseline is obtained by dropping the sample previously completely cured and cooled down at room temperature into the calorimeter. For calculation, the reference baseline is obtained by taking 0 for the constant rate.

The total heat flux is drawn as a function of time in Fig. 1, as obtained from calculation. The very high value of the heat flux obtained at the beginning of the process, just after the introduction of the sample should be noted. The negative heat flux corresponds to the intense heating of the sample; this cannot be observed by experiment.

As it is not possible to distinguish the exothermal part of the heat flux in Fig. 1, we have drawn the same curve with different scales for the coordinates, especially for the heat flux. The curve obtained in this way (Fig. 2) is the heat flux–time history usually recorded in experiment.

The enthalpy of cure can be obtained by measuring the area under the positive part of the exotherm obtained from experiment. However, as illustrated in Fig. 3, the reaction takes place in the sample (especially near the surface) as soon as the sample is introduced into the calorimeter. Unfortunately, it is not possible to study this because the values of the heat flux during the endothermic part of the reaction are too high. However, the total heat flux–time history is easily supplied from calculation with the help of the model. The difference between the heat flux obtained with the fresh

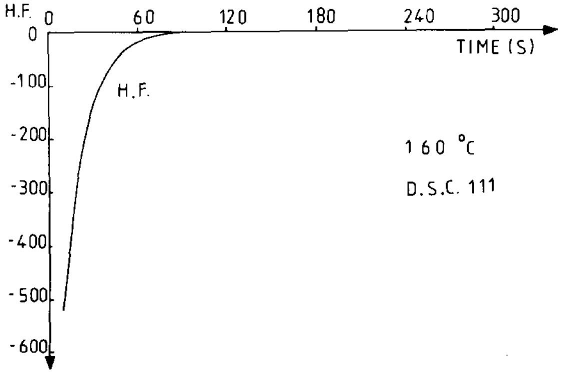

Fig. 1. Total heat flux–time history in DC calorimetry at 160 °C.

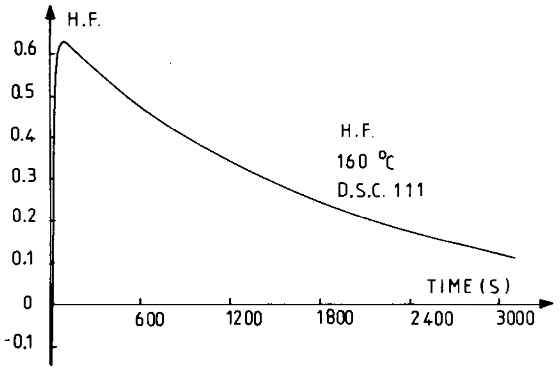

Fig. 2. Positive part of the heat flux–time history in DC calorimetry at 160° C.

uncured rubber and the heat flux due to the heating of the pre-cured rubber can then be used to determine, the total heat flux accompanying the reaction of cure as shown in Fig. 3. This result is interesting essentially for the following reasons.

(i) The first part of the reaction of cure cannot be determined by experiment, although this part is especially important for reactions having some initiation steps.

(ii) As a part of the enthalpy is lost, the enthalpy of cure obtained from DC experiments must be always lower than that determined using DSC.

(iii) The highest temperature at which measurement can be obtained is determined by the induction period required for initiation of the cure reaction, following the case (i).

(iv) The lowest temperature for cure studies is determined by the calorimeter sensitivity i.e. the rate of enthalpy change cannot be recorded if the cure rate is too small.

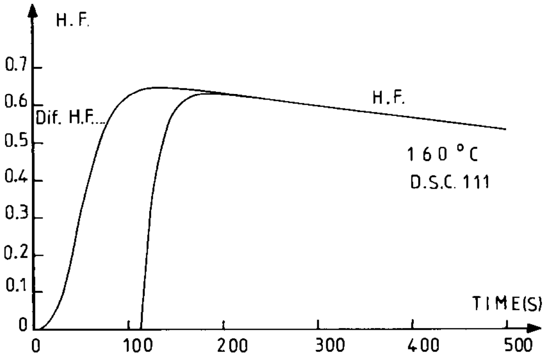

Fig. 3. Positive part of the heat flux–time history (H.F.). Difference in the heat flux obtained with reaction and without reaction (Dif. H.F.). DC at 160° C.

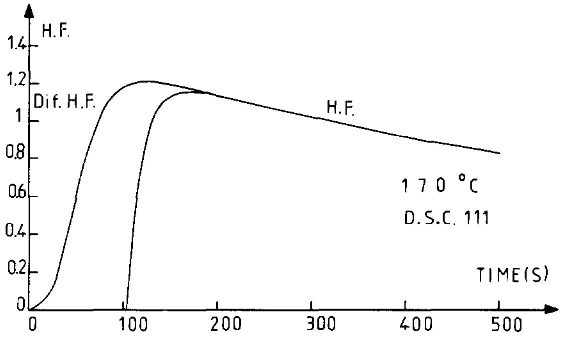

Fig. 4. Positive part of the heat flux–time history (H.F.). Difference in the heat flux obtained with reaction and without reaction (Dif. H.F.). DC at 170°C.

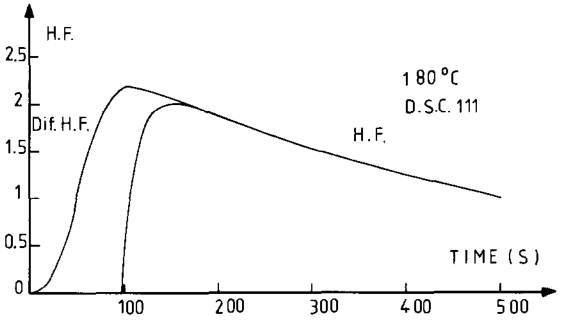

Fig. 5. Positive part of the heat flux–time history (H.F.). Difference in the heat flux obtained with reaction and without reaction (Dif. H.F.). DC at 180°C.

TABLE 3

Enthalpy of cure in DC

Temperature of calorimeter (°C)	160	170	180
Enthalpy lost (%)	4.8	7	12.6

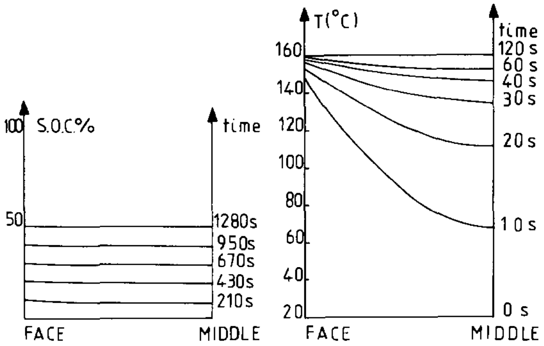

Fig. 6. Profiles of temperature (right) and SOC (left) developed within the sample in DC calorimetry at 160°C.

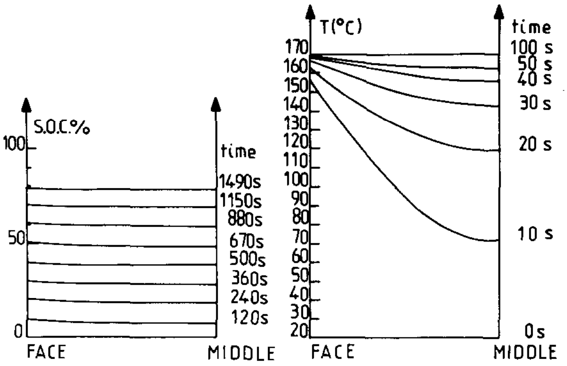

Fig. 7. Profiles of temperature (right) and SOC (left) developed within the sample in DC calorimetry at 170 ° C.

The amount of heat lost during the intense heating of the sample at the beginning of the process, depends largely on the value of the constant temperature chosen for the calorimeter. This is illustrated in Figs. 3–5 where the temperature ranges from 160–180 ° C, and is demonstrated in Table 3 where the heat lost is shown to increase with the temperature of the calorimeter.

Profiles of temperature and state of cure

The profiles of temperature and state of cure obtained from calculation are presented in Figs. 6–8 for temperatures ranging from 160 to 180 ° C. As shown, the time required for the sample to establish thermal equilibrium after the sample is introduced into the calorimeter is not negligible, being of the order of 2 min. During this period of time, the set calorimeter temperature is not the true sample temperature because of the high gradients of

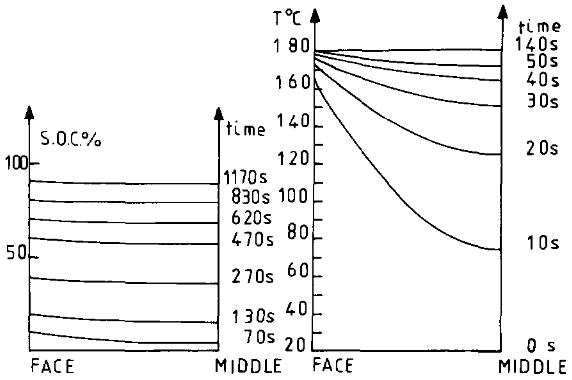

Fig. 8. Profiles of temperature (right) and SOC (left) developed within the sample in DC calorimetry at 180 ° C.

temperature developed within the sample. As a result, two main disadvantages of the DC technique are seen: (i) a temperature window with a narrow width (20 ° C) is found over which meaningful data can be obtained, located between the lowest and the highest temperatures as defined earlier; (ii) whatever the temperature chosen in this window, the first part of the exotherm is not obtained, and the important induction period of initiation of the cure reaction is lost.

Calorimetry in the scanning mode

In the DSC technique, the sample of fresh uncured rubber is scanned at the selected heating rate up to a temperature at which the reaction exotherm is complete. The enthalpy changes associated with the chemical reaction are monitored as a function of temperature. After the rubber has been given this first cure, it is cooled down to room temperature with the calorimeter, and then scanned under conditions identical to the initial scan. In the second DSC curve, no exotherm is observed in the cure temperature range when the first cure has been completed, and the curve thus obtained is then the reference baseline.

Heat flux–temperature history

For a given sample size, the main parameter in the DSC technique is the heating rate. The heating rate has various effects on the heat flux–temperature histories, as shown in Fig. 9.

(i) An increase in the heating rate is responsible for a retardation in the heat flux towards the highest temperature; this is especially important for the maximum of the heat flux.

(ii) The heat flux describing the rate of the reaction starts at about the same temperature, for all heating rates.

(iii) The sensitivity of the technique, measured by the height of the heat flux at its maximum, is directly proportional to the heating rate (see Fig. 11).

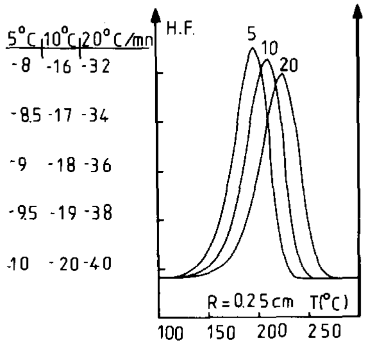

Fig. 9. Calorimetry in scanning mode. Effect of heating rate on the heat flux–temperature history.

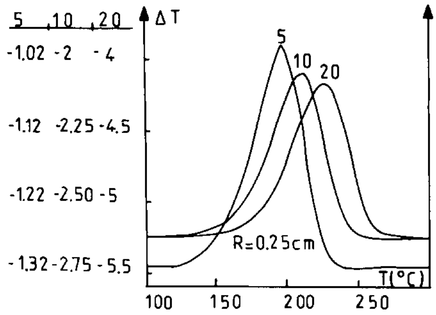

Fig. 10. Calorimetry in scanning mode. Effect of heating rate on the difference between the temperature on the face and at the middle of the sample (T).

Profiles of temperature during the process

Some gradients of temperature are developed during the process, for two reasons.

(i) Because of the low heating rate through the rubber, the temperature of the middle of the sample is slow to rise with reference to the temperature of the calorimeter, and no reaction occurs. This has been studied in previous work by considering not only the heating rate but also the sample size [3]. It has been proved that the difference between the temperature on the face and at the middle varies as a linear function of the heating rate and of the square of the radius of the sample.

(ii) As a result of the internal heat generated from the cure reaction, other gradients are developed and superimposed on the first gradients. The difference between the temperature at the middle and on the face is shown in Fig. 10 as a function of the temperature of the calorimeter. This difference of temperature (ΔT) is found to vary linearly with the heating rate (Fig. 11).

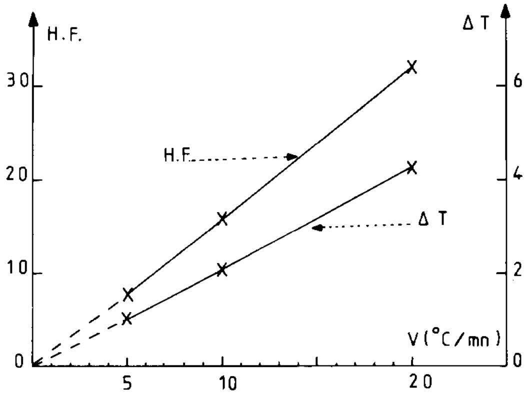

Fig. 11. Effect of heating rate on the height of the maximum heat flux, and on the maximum value of the difference between the temperature on the face and at the middle of the sample.

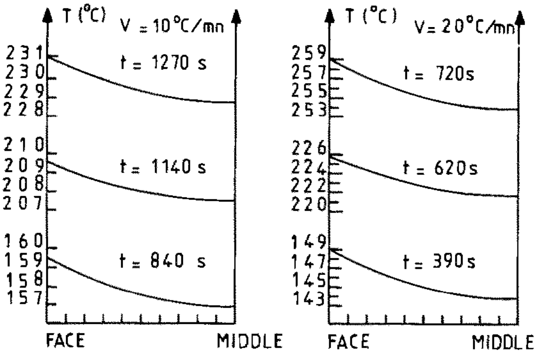

Fig. 12. Gradients of temperature developed within the sample radius at various times, for two heating rates: left, 10 °C min^{-1}; right, 20 °C min^{-1}. Bottom, before the maximum heat flux–temperature curve; middle, at the maximum value of the heat flux; top, at the end of the maximum of heat flux–temperature curve.

Because of the contribution of the heating in scanning mode and the heat generated from the exothermic reaction, the gradients of temperature obtained through the radius of the sample are rather complex. Some of these gradients are shown in Fig. 12 for two values of the heating rate, 10 °C min^{-1} (left) and 20 °C min^{-1} (right); they have been calculated in three positions along the heat flux–time curve, before the beginning of the maximum of this curve, at the maximum, and after the maximum has arisen. As shown, the effect of the heating rate on the temperature gradients is important, since these gradients are proportional to the heating rate [3]. When the enthalpy of reaction is low, as in rubber cure, the effect of the exothermic reaction on the development of the profiles of temperature in the sample is rather small.

CONCLUSIONS

Many workers prefer to use the DC technique rather than calorimetry using the scanning mode for studying the kinetics of reactions, essentially because the temperature should be constant using DC, which simplifies the kinetic study.

The purpose of this paper has been to show some of the main disadvantages of DC. These are particularly important for reactions with a first induction period as for instance the cure of rubber. Two points must be considered. The temperature of the sample is not the set calorimeter temperature especially during the first period of heating after the sample is placed in the oven, and some important temperature gradients are developed in the sample. Since it takes time for the sample to establish thermal equilibrium after introduction to the calorimeter, the first part of the reaction is lost, and the induction period of the cure cannot be studied. Moreover, the enthalpy of reaction measured using DC is lower than the value obtained by DSC, because a part of the reaction takes place during the heating period of the sample.

It must be remembered that even, in DSC, some temperature gradients are developed within the sample during the heating period. These gradients become constant after a certain period [3]. However, these temperature gradients being proportional to the heating rate, can be controlled by choosing an appropriate heating rate.

LIST OF SYMBOLS

C	specific heat of rubber
HF	heat flux transferred through the sample surface
M	modulus
Q_t	heat evolved from cure reaction up to time t
Q_∞	enthalpy of cure
r	radius of circle
R_s	radius of sample
Δt, Δx	increments of time, and space
$T_{i,r}$	temperature at time $i\Delta t$ and in the ring between $r-(\frac{\Delta r}{2})$ and $r+(\frac{\Delta r}{2})$

Greek letters

ρ	density of rubber
λ	thermal conductivity of rubber
α	thermal diffusivity of rubber

REFERENCES

1 D.W. Brazier, in N. Grassie (Ed.), Developments in Polymer Degradation, Vol. 3, Applied Science Publishers, London, 1981, p. 27.

2 M. Chater, D. Lalart, F. Michel-Dansac and J.M. Vergnaud, Eur. Polym. J., 22 (1986) 805.

3 J.Y. Armand, R. Gonnet, R. Jones, J. Bouzon, M. Touchard and J.M. Vergnaud, Thermochim. Acta, 103 (1986) 341.

4 A. Acetta and J.M. Vergnaud, Rubber Chem. Technol., 56 (1983) 689.

5 A. Sadr, R. Granger and J.M. Vergnaud, J. Appl. Polym. Sci., 29 (1984) 955.

6 M. Chater and J.M. Vergnaud, Eur. Polym. J., in press.

7 J.A. Nixon and J.M. Hutchinson, Plast. Rubber Process. Applic., 5 (1985) 349.

8 S.Y. Pusatcioglu, J.C. Hassler, A.L. Frickle and H.A.Mc Gee, J. Appl. Polym. Sci., 25 (1980) 381.
9 M.R. Barone and D.A. Caulk, Int. J. Heat Mass Transfer, 22 (1979) 1021.
10 P.K. Mallick and N. Raghupathi, Polym. Eng. Sci., 19 (1979) 774.
11 A. Khouider, J.B. Rochette and J.M. Vergnaud, Thermochim. Acta, 89 (1985) 81.
12 A. Khouider, J.B. Rochette and J.M. Vergnaud, Thermochim. Acta, 89 (1985) 93.
13 A. Khouider, J. Bouzon and J.M. Vergnaud, Thermochim. Acta, 98 (1986) 285.
14 G. Chataing, M. Chater and J.M. Vergnaud, Thermochim. Acta, 89 (1985) 107.
15 M. Chater, G. Chataing and J.M. Vergnaud, Thermochim. Acta, 89 (1985) 119.
16 M. Chater, G. Chataing and J.M. Vergnaud, Thermochim. Acta, 90 (1985) 135.
17 A. Acetta, P. Le Parlouer and J.M. Vergnaud, Thermochim. Acta, 59 (1982) 149.
18 S.K. Bhatnagar and S. Banerjee, J. Inst. Rubber Ind., 2 (1968) 177.
19 N. Bekkedahl and J.J. Weeks, J. Res. Natl. Bur. Stand., Sect. A, 73 (1969) 221.