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DETERMINATION OF HEAT FLUX AND PROFILES OF TEMPERATURE AND STATE OF CURE IN ISOTHERMAL CALORIMETRY WITH REACTION OF HIGH ENTHALPY

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ABSTRACT

The sample is studied while heated in a calorimeter working under isothermal conditions. Because of the local heating arising from exothermic reactions and low heat transfer through the sample, the sample temperature during cure is not the temperature of the calorimeter. The profiles of temperature and state of cure developed through the sample during the cure are calculated, as well as the heat flux evolved through the sample–calorimeter vessel interface. The shape of heat flux–time curves obtained by calculation are in agreement with the shape of experimental curves. It is now possible to compare and correlate the following data obtained simultaneously as a function of time: heat flux, profiles of temperature and state of cure through the sample section. The effect of the heat transfer coefficient between the sample and calorimeter vessel is pointed out, as well as that of the calorimeter temperature.

INTRODUCTION

Numerous thermoanalytical methods have been developed to characterise the cure process of epoxide resins. In both DSC and DC techniques, the enthalpy changes accompanying the chemical reaction 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 at a known linear rate (DSC) or as a function of time, the calorimeter being held at constant temperature (DC). The information that can be obtained from such profiles on the curing process is of interest. Detailed kinetic analysis of the enthalpy profiles is only possible, however, in the case of the simplest of reactions, and the determination of meaningful kinetic parameters for a complex reaction is not feasible. In fact, it must be emphasised that, although these methods are not in their infancy, some limitations in experimental technique and data interpretation are apparent.

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One source of error arises from heat transfer from the specimen to the reference cell [1,2], which particularly applies for reactions of high enthalpy. The applied temperature is the set calorimeter temperature and not the true sample temperature during cure, because of local heating arising from the exothermic reactions and low heat transfer through the sample [3,4].

Moreover, reactions do present some specific problems both in sample handling and in obtaining reproducible experimental results. On the one hand, in sample preparation it is imperative, for example, that good contact is made between the sample, the sample holder and the oven [5,6]. On the other hand, the small sample size used in DSC necessitates that all ingredients in the sample are well dispersed. Dispersion problems do occasionally arise and will generally be observed by lack of reproducibility. The question which always arises is how representative is a 10–100-mg sample, taken from a large batch, of the homogeneity of the batch.

In this paper a new approach in such studies based on differential calorimetry (DC) is explored. We have chosen this method because the enthalpy versus time profile obtained under such conditions approximates the time scale of the production process more closely. Our method is developed for predicting the profiles of temperature and state of cure developed throughout the sample as well as the heat flux transferred from the sample to the calorimeter detector, during the cure process. The problem is solved by using a numerical method with finite differences [7] applied to the cylindrical sample. The model takes into account the kinetics of heat evolved by cure reaction and heat transfer through the sample and oven–sample interface. In this paper as throughout a paper published earlier [6], the kinetic parameters have been kept constant in order to simplify the study. Although the cure of epoxy resins is a complex chemical process, the heat of overall reaction is described by an nth-order reaction with a single activation energy.

THEORETICAL

Mathematical treatment

The following relations involve the kinetic parameters, such as: rate constant, K_0; order of overall reaction, n; activation energy, E; and parameters characterizing heat transfer, such as: thermal conductivity, λ; density, ρ; and specific heat of the body (epoxy resin); its shape and size; and the external conditions, including the temperature of the surroundings (oven block or heat-flux detector of calorimeter) and the coefficient of heat transfer between surroundings and the surface of the sample.

Before developing the model of the cure process, different basic assumptions are made for the sample: no flow, no molecular diffusion, radial heat conduction, longitudinal heat conduction is neglected, the flow of heat takes place in a plane perpendicular to the axis, and the lines of flow are radial.

The equation of transient heat conduction through the sample, when expressed in cylindrical coordinates, reduces to

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

because the temperature is only a function of radial abscissa, r, and time, t, following the above assumptions.

Although the cure reaction of epoxide resin is a very complex chemical process, the overall rate of cure is given by the single expression

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

where the heat of reaction evolved up to time t is a function of position r.

Initial and boundary conditions are as follows

$$t=0 \quad 0\leqslant r\leqslant R_s \quad T=T_r \quad \text{sample space} \tag{3}$$

$$\begin{array}{llll} t>0 & r\geqslant R_s & T=T_m & \text{oven space} \\ & 0\leqslant r<R_s & T=T_{r,t} & \text{rubber space} \end{array} \tag{4}$$

Numerical analysis

Equations (1) and (2) cannot be solved by a mathematical treatment because of the presence of internal heat of reaction. The solution is obtained by using an explicit numerical method. By considering a plane perpendicular to the axis of the cylinder, the circular cross-section can be divided into several circles of radius r, $r+\Delta r$, $r+2\Delta r$, etc., r being between 0 and R_s (the radius of the cylinder).

The temperature on the circle of radius r and at the time $(i+1)\Delta t$, after the elapse of a finite time increment is defined by eqn. (5) as a function of the temperature at the preceding time $i\Delta t$ on circles of radius r, $r+\Delta r$ and $r-\Delta r$.

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

Equation (5) is not available for the determination of temperature in the middle of the cylinder. Equation (6) can be used for calculating the temperature for $r=0$, as a function of temperature on the first circle of radius Δr and in the middle of the cylinder at the preceeding time.

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

A heat balance at the cylinder face gives

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

where R_s is defined by the relation

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

The modulus M is the dimensionless number

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

The heat flux emitted from the cylinder to the heat flux detector can be obtained from the following equation.

$$\text{Heat flux} = \lambda_s \frac{T_{R_s} - T_{R_s - \Delta r}}{\Delta r} \tag{10}$$

The internal heat generated by the cure reaction per unit volume at the time $(i+1)\Delta t$ during the time Δt, is calculated by the recurrent relation

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

with

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

and

$$Q_i = \sum_{i=0}^{i} \left(\frac{dQ}{dt}\right)_i \Delta t \tag{13}$$

EXPERIMENTAL

The apparatus [8] (DSC 111, Sétaram) can work either in isothermal or in scanning mode. In the present work concerned with isothermal tests, the DSC is stabilized at the working temperature, and both holders (for measurement and reference) are simultaneously introduced as quickly as possible into the sensitive zone. The holder is located in the calorimetric block which functions as a heat sink. The temperature of the block is controlled. A heat-flux detector, consisting of conductive 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 detector emits a signal which is proportional to the heat transferred per unit of time.

After cure in the DSC vessel, the sample is extracted from the vessel, cooled at room temperature, and reheated in the DSC vessel under the same

TABLE 1

Values of parameters

Kinetic reaction	$n = 1$; $K_0 = 300000\ \mathrm{s}^{-1}$; $E = 15\ \mathrm{kcal\ mol}^{-1}$
Heat transfer	$\lambda = 10^{-3}\ \mathrm{cal\ s}^{-1}\ \mathrm{cm}^{-1}\ \mathrm{deg}^{-1}$; $C = 0.32\ \mathrm{cal\ g}^{-1}\ \mathrm{deg}^{-1}$; $\alpha = 25 \times 10^{-4}\ \mathrm{cm}^2\ \mathrm{s}^{-1}$
Enthalpy of cure	$Q_\infty = 65\ \mathrm{cal\ g}^{-1}$
Sample	$R_s = 0.35$ cm; $T_i = 20$°C; $T_m = 130$–140–150°C
Calculation	$\Delta r = 0.025$ cm; $\Delta t = 0.05$ s; $H = 1$–20

conditions, to give the temperature dependence of the specific heat of the cured sample as formed after the initial DC experiment. This new curce can be superimposed on the initial curve to give the baseline which would be observed in the absence of cure.

In sample preparation, it is imperative that good contact was made between the epoxide sample and the holder, as well as between the holder and the calorimetric vessel. These points are obviously of great importance, and will certainly be a limitation for the development of the technique. About 100 mg of the compound is encapsulated in the holder. A smaller size would necessitate that all ingredients in the sample were well dispersed.

Throughout this paper, the kinetic and heat transfer parameters are kept constant in order to simplify the study. The values obtained for these parameters are shown in Table 1. They are in good agreement with some of the values published in earlier literature [9–13].

RESULTS

Effect of the heat transfer between the holder and the calorimetry vessel

Figure 1 illustrates a typical calorimeter curve obtained for the cure of epoxide resin with the help of DSC working under isothermal conditions at 150°C. Several heat flux curves are calculated by using different values for the coefficient of heat transfer between the holder (or sample surface) and the calorimetry vessel. The value of H seen in eqn. (8) is directly related to the above coefficient of heat transfer, and the quality of the contacts between the sample and holder, and also between the holder and the calorimetry vessel. For instance, a value of 1 for H corresponds with a contact like that occurring in the resin–resin interface with perfect contact; the value of 20 characterises the heat transfer through an iron mold–resin interface. Up to now, it has not been possible to determine the value of this coefficient in the case at hand precisely.

The value given for the coefficient H has a quantitative effect on the value of the heat flux obtained in the calorimeter. The lower the value of H,

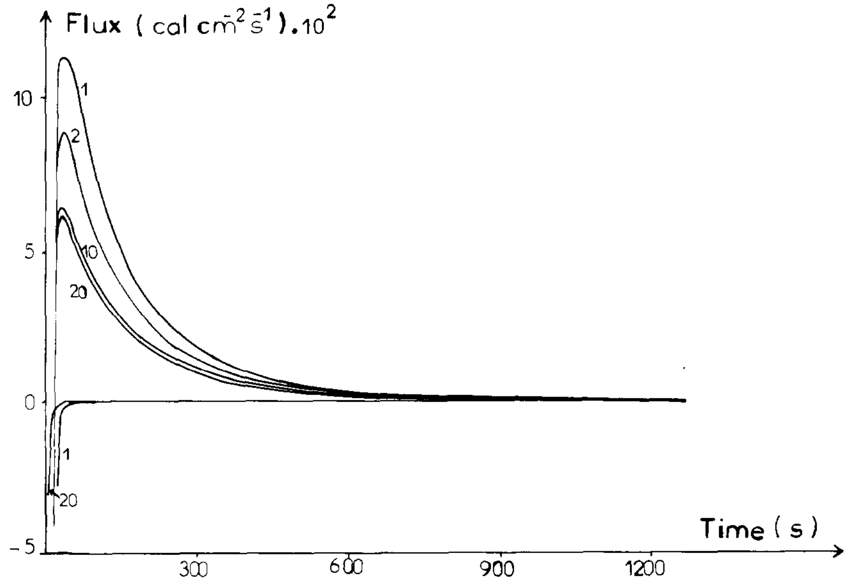

Fig. 1. Heat flux vs. time calculated at 150°C for different values of heat transfer through calorimetry vessel–sample interface. $H = 1–5–10–20$.

the higher the sensibility measured for the heat flux. In fact, the effect of a variation of H on the magnitude of heat flux is only very important for low values of H; this effect becomes insignificant when H is between 10 and 20.

Fortunately, there is no effect of the value of R on the quality of contact between the holder and the calorimetry vessel on the shape of the heat flux curves. Thus, kinetic treatments of these curves are not altered by the value of the coefficient H.

After the sample has been given a pre-cure, it is quench-cooled to prevent further reactions and then heated under conditions identical to the initial heating. This second step is calculated with the help of the model described above by taking a value of 0 for the constant rate K_0.

Another effect of the magnitude of the coefficient H can be appreciated from Fig. 1. It is concerned with a very small retardation in the time at which the reaction starts and develops through the mass.

The calculated and experimental curves have, on the whole, approximately the same shape.

Profiles of temperature and SOC developed through the sample

The foregoing discussion has been concerned with the heat flux occurring during the cure of epoxide resin, and the effect of heat transfer through the sample–calorimetry vessel interface has been especially pointed out and studied.

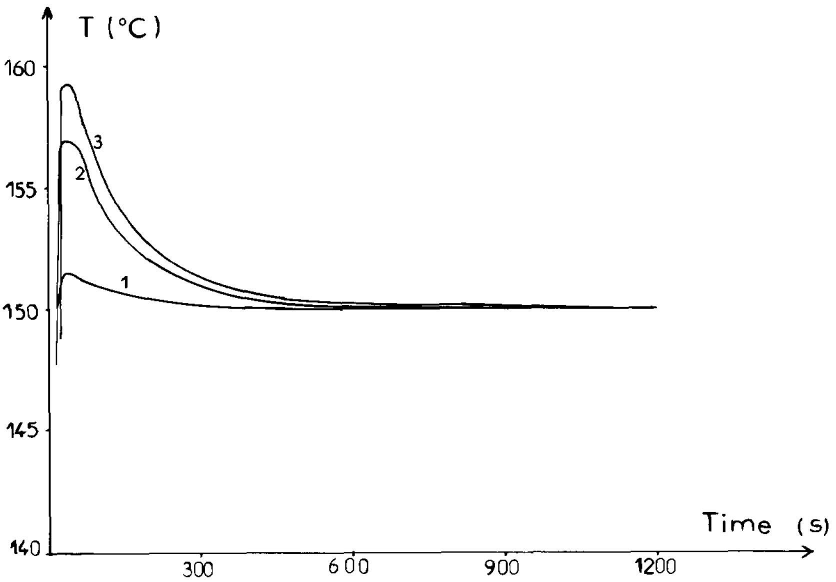

Fig. 2. Temperature vs. time obtained at 150°C in different places across the sample section. (1) Face; (2) $r = R_s/2$; (3) middle, $H = 1$.

Because of the low heat transfer through the sample itself, profiles of temperature and SOC can be seen through the epoxide resin sample and calculated. As the enthalpy change is exothermic, actual constant conditions

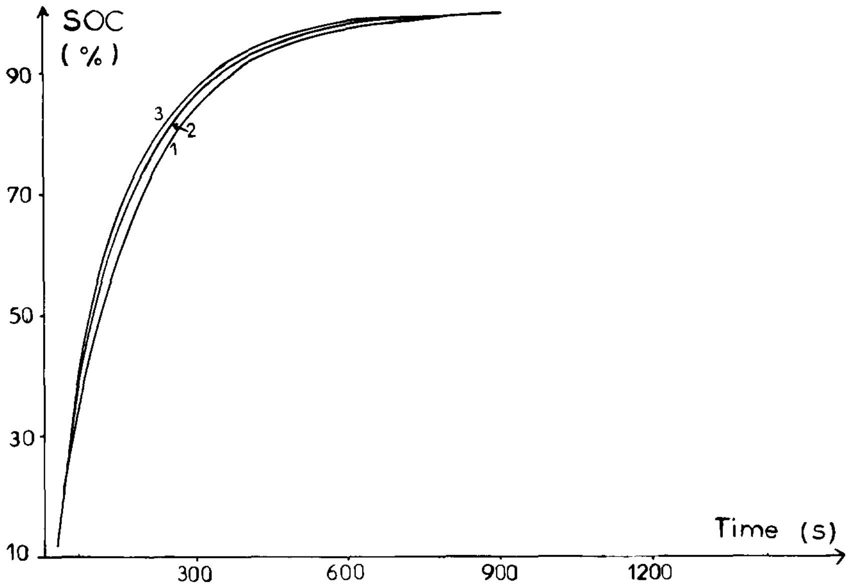

Fig. 3. SOC vs. time at 150°C in different places across sample section. (1) Face; (2) $r = R_s/2$; (3) middle, $H = 1$.

are not possible in the sample itself during cure reactions. In fact, the temperature rise accompanying the process is the variable determined in DTA and the basis for earlier thermocouple techniques.

The profiles of temperature developed through the sample can be appreciated in Fig. 2 where the temperature–time history is shown in different places on the sample. These calculations have been done by giving a value of 1 to the heat transfer coefficient, *H*. These profiles are quite different, proving the absence of homogeneity in the sample heated under these above conditions. A difference of about 8° between the middle and face of the sample can be seen for the maximum value reached by the temperature.

The different values for the state of cure across the section are illustrated in Fig. 3. These results show that gradients of SOC through the section are developed as soon as the maximum temperature is reached, and maintained for about 500 s. Of course, the higher SOC value is obtained in the middle where the temperature is higher. The difference between the extreme SOC values across the section does not exceed 7%, but it is very significant.

Effect of the temperature on the experiments

Figure 4 illustrates typical heat flux curves obtained by calorimetry for the cure of epoxide resin at different temperatures: 130, 140 and 150°C. These curves have been calculated by taking the same value for H ($H = 1$). The following known results, concerning the experimental limitation on the

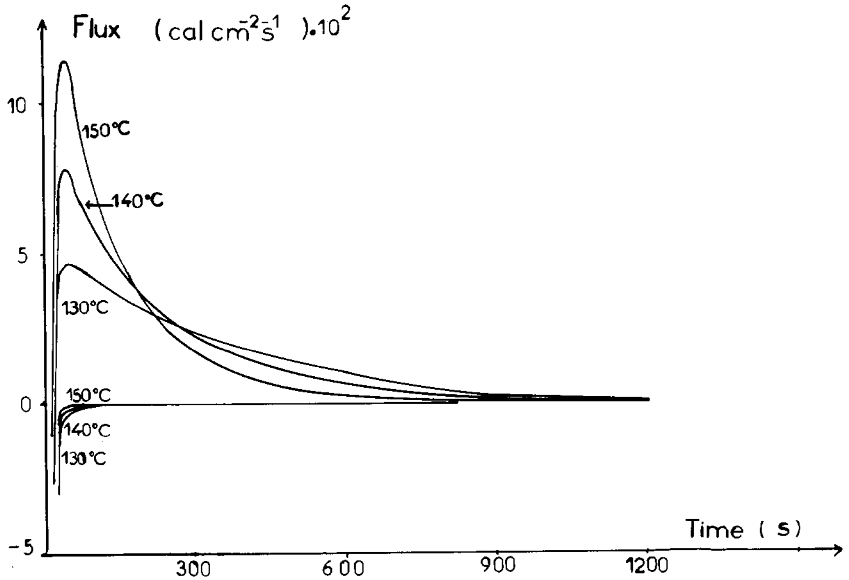

Fig. 4. Heat flux vs. time obtained for different temperatures of the calorimeter: 130–140–150°C, $H = 1$.

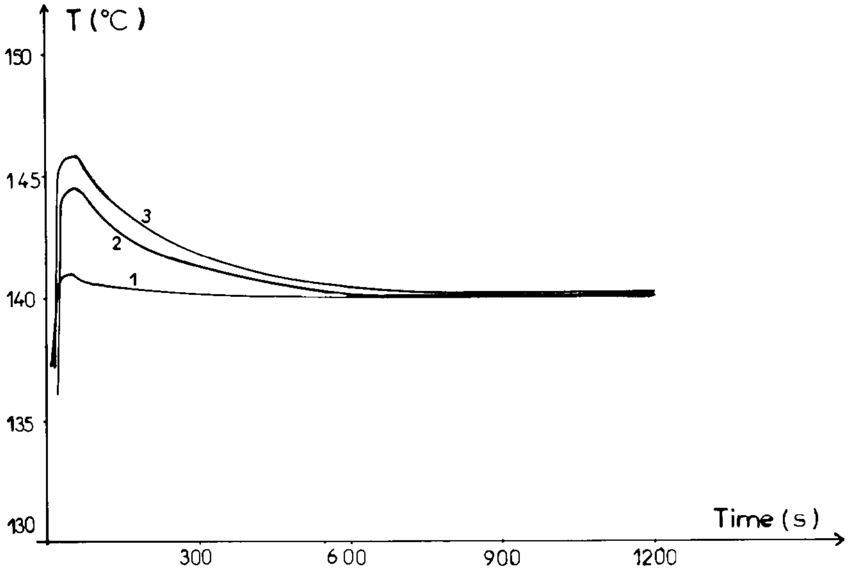

Fig. 5. Temperature vs. time obtained at 140°C in different places across sample section. (1) Face; (2) $r = R_s/2$; (3) middle, $H = 1$.

temperature range over which meaningful data can be obtained, are clearly shown. The lowest possible temperature for cure studies is limited by the calorimeter sensitivity. When the cure rate is very low, the rate of enthalpy

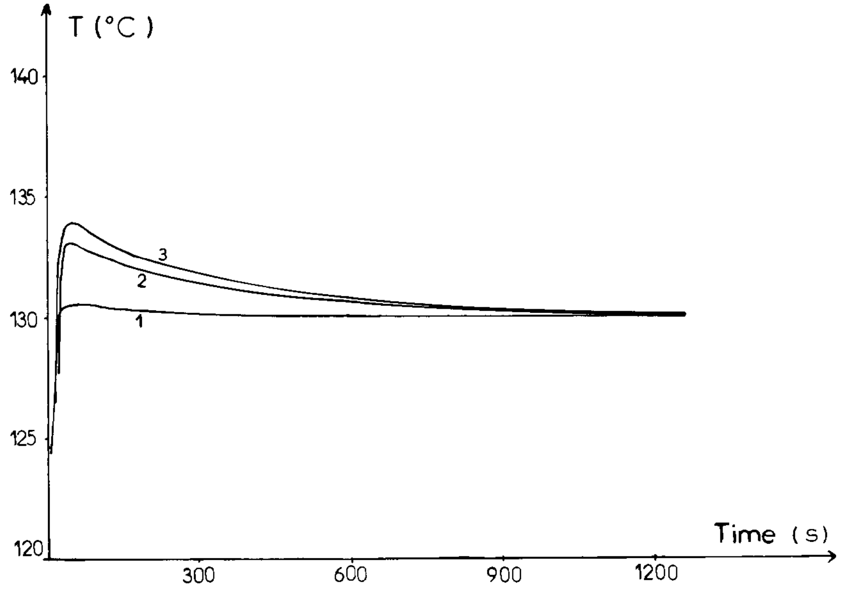

Fig. 6. Temperature vs. time obtained at 130°C in different places across sample section. (1) Face; (2) $r = R_s/2$; (3) middle, $H = 1$.

TABLE 2

Effect of calorimetry temperature on temperature heterogeneity across the sample section

Calorimeter	Face	$r = R_s/2$	Middle
130	0.05	1.5	2.0
140	1.15	4.5	5.75
150	1.5	6.9	9.25

change is too small to be recorded. The highest temperature at which measurements can be obtained is determined by the length of the induction period for the cure reaction to initiate. If the induction period is shorter than the time required for the calorimeter to establish thermal equilibrium after the sample is introduced, this first part of the cure exotherm cannot be obtained.

The effect of the calorimeter temperature on the gradients of temperature developed through the sample is shown in Fig. 2 at 150°C, Fig. 5 at 140°C and Fig. 6 at 130°C. Table 2 contains the largest differences in the temperature of the sample for these calorimeter temperatures. They are expressed as the difference between the sample temperature and the constant calorimetry temperature at different places across the sample section.

The heterogeneity in the state of cure across the sample section can also be compared in Fig. 7 for 140°C and Fig. 8 for 130°C. The largest

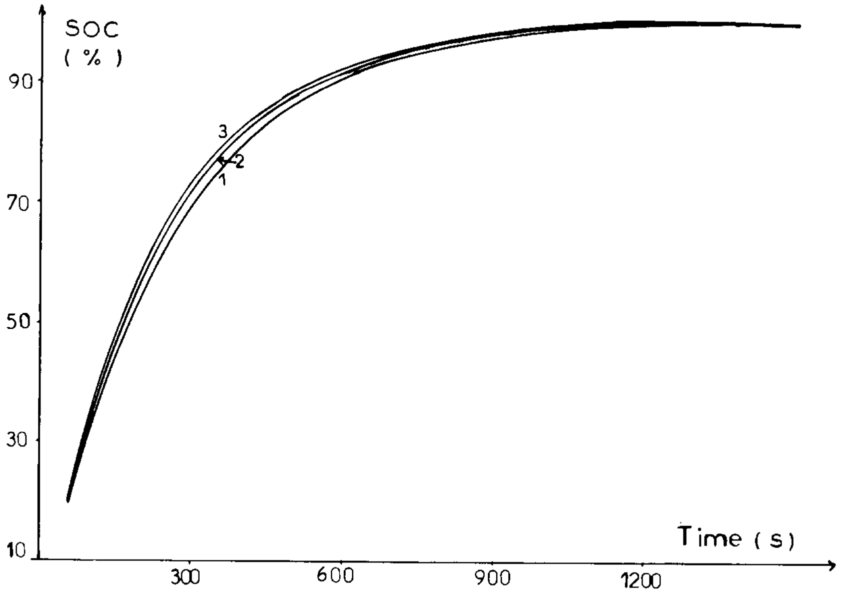

Fig. 7. SOC vs. time at 140°C in different places across sample section. (1) Face; (2) $r = R_s/2$; (3) middle, $H = 1$.

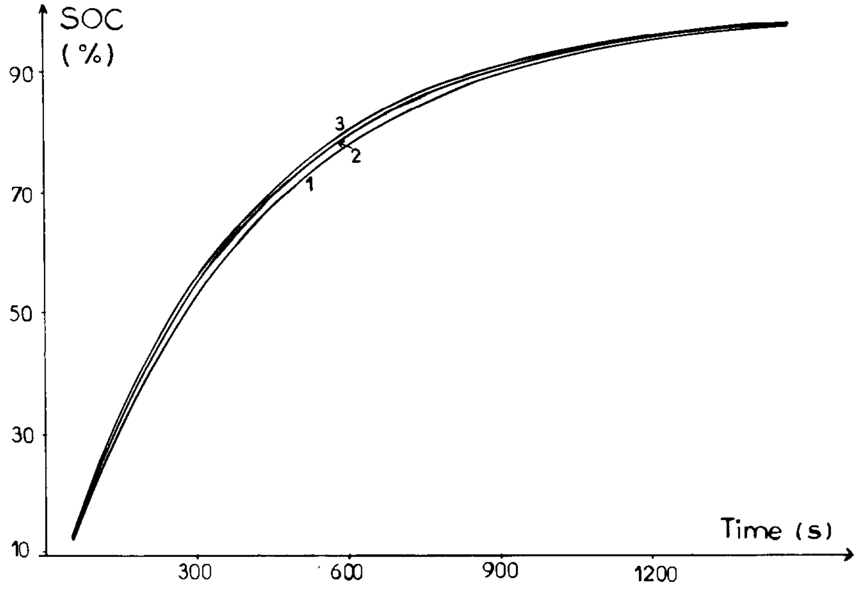

Fig. 8. SOC vs. time at 130°C in different places across sample section. (1) Face; (2) $r = R_s/2$; (3) middle, $H = 1$.

TABLE 3

Largest difference in SOC

Calorimeter	Time	ΔSOC
130	330	2.7
140	210	4.2
150	120	6.3

differences between the state of cure obtained at the face and in the middle of the sample are indicated in Table 3, as well as the time at which they are obtained.

CONCLUSIONS

The utilisation of DC in the study of the cure of epoxide systems has been explored in this paper. The objective has been to relate the observed enthalpy changes to known events that are occurring in the cure reaction (profile of temperature and state of cure developed through the sample), particularly when they are related to a practical industrial process.

Although at first sight the use of reaction calorimetry techniques to study such complex processes may appear feasible, the determination of detailed kinetics is not easy in practice. Where chemical reactions occur during the heating period, as in the cure of epoxide resins, heat transfer plays a particularly important role, because the rate of the reaction increases rapidly with small increases in temperature. Another point certainly worth noting is the quality of the contact between the sample and holder, and, perhaps overall, that between the holder and the calorimetry vessel.

Considerably more work is needed in the quantitative interpretation of the observed enthalpy profiles for determining the kinetic parameters of the reaction. However, the groundwork has been laid in this first paper, and wider applications of calorimetric procedures are expected in the future.

LIST OF SYMBOLS

ρ	density of epoxide resin
C	specific heat of epoxide resin
λ_s	thermal conductivity of epoxide rubber
λ_m	thermal conductivity of metal
T	temperature
t	time
R_s	radius of the cross-section of the sample cylinder
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
Δx	finite increment in radius
α	thermal diffusivity
n	order of overall cure reaction
K_0	rate constant of reaction
E	activation energy

REFERENCES

1 T.R. Manley, in J. Chiu (Ed.), Polymer Characterization by Thermal Methods of Analysis, Dekker, New York, 1974, p. 53.
2 D.W. Brazier, in N. Grassie (Ed.), Developments in Polymer Degradation, Vol. 3, Applied Science Publishers, London, 1981, p. 27.
3 A. Accetta, P. Le Parlouer and J.M. Vergnaud, Thermochim. Acta, 59 (1982) 149.
4 A. Accetta and J.M. Vergnaud, Rubber Chem. Technol., 56 (1983) 689.
5 J.B. Rochette, J. Bouzon and J.M. Vergnaud, Thermochim. Acta, 85 (1985)in press.
6 M. Abdul, B. Rochette, A. Sadr and J.M. Vergnaud, Thermochim. Acta, 80 (1984) 287.
7 A. Accetta, G. Gangnet, L. Vincent and J.M. Vergnaud, 3rd Int. Conf. Computers and Chemical Engineering, Paris, 1983.
8 J. Mercier, J. Therm. Anal., 14 (1978) 161.
9 A. Dutta and M.E. Ryan, J. Appl. Polym. Sci., 24 (1979) 635.
10 S. Sourour and M.R. Kamal, Thermochim. Acta, 14 (1976) 41.
11 J. Mijovic, Kim Jinhwan and J. Slaby, J. Appl. Polym. Sci., 9 (1983) 1449.
12 R.P. Kreahling and D.E. Kline, J. Appl. Polym. Sci., 13 (1969) 2411.
13 S. Sourour and M.R. Kamal, Polym. Eng. Sci., 16 (1976) 480.