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EFFECT OF SAMPLE SIZE AND HEATING RATE ON THE DSC PROCESS FOR REACTIONS OF HIGH ENTHALPY

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ABSTRACT

Various parameters are of interest in differential scanning calorimetry (DSC): the enthalpy of reaction, the heating rate and the sample size. In this study the two latter parameters were considered fundamentally, by choosing the cure reaction of epoxy resin which has a high enthalpy. Two samples, of different size and cylindrical in shape, were studied with various heating rates ranging from 1 to 5 °C min^{-1}. The heat flux determined in various places was found to be proportional to the heating rate and to the radius of the sample. The difference in temperature was determined between the middle and the face of the samples. This difference in temperature was found to be proportional to the heating rate and to the square of the radius of the sample. These results were attained by calculation with the help of a numerical model based on an explicit method with finite differences. The model took into account not only the heat transferred by conduction through the sample, but also the heat evolved from the cure reaction.

LIST OF SYMBOLS

C	specific heat
E	activation energy
HF	heat flux
k_0	rate constant of reaction
M	dimensionless factor
n	order of reaction
Q_t	enthalpy evolved up to time t
Q_∞	enthalpy of reaction
R	radius of sample
r	radius of circumference
Δr	finite increment in radius
T	temperature
t	time
Δt	finite increment in time
v	heating rate

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α	thermal diffusivity
λ	thermal conductivity
ρ	density of sample

INTRODUCTION

The kinetics of cure have been determined by calorimetric methods for reactions of high and low enthalpy. The profile of the rate of enthalpy change is obtained as a function of time when the calorimeter is held at constant temperature (DC), and as a function of temperature as the sample is heated at a known linear rate (DSC) [1]. Because of the low thermal conductivity of polymers and resins, some temperature gradients were found to develop through the sample [2,3]. Other temperature gradients are a result of the rate of reaction [4]. Owing to these temperature gradients, the temperature in the sample is found to be different from that of the calorimeter.

In order to study these calorimetric techniques and to gain a fuller insight into the process occurring in the sample, some experimental and theoretical studies were carried out for DC and DSC [5,6]. The cure reaction of epoxy resin which has a high enthalpy was used. No fault was found with these techniques of calorimetry. The heat flux–temperature and heat flux–time histories were taken into account. By taking into consideration not only the kinetics of cure but also the heat transferred through the sample by conduction, some numerical techniques based on numerical analysis were derived and were shown to agree with experiment. Taking advantage of these models, the profiles of temperature and state of cure developing through the sample were obtained. The cure process in the calorimetric sample was rather complicated, and was related to various parameters. The sample size and heating rate were the most important parameters in DSC [4,7], and the cure enthalpy was important in the low enthalpy cure of rubber [8].

The influence of the sample size was found to be of great relevance [1], especially when solid state mixtures were studied. The question which always arose was how representative of the homogeneity of the batch was a small sample taken from the batch. Larger samples, when subjected to high heating rates in DSC, could easily develop high untimely temperature gradients within the mass due to the low thermal conductivity of the material and to the enthalpy of cure. The following three cases were examined:

(i) No reaction took place in the sample, and the temperature at the middle of the sample was found to lag behind that of the calorimeter, this retardation being proportional to the heating rate and to the square of the dimension of the sample (the radius for the cylindrical sample) [3].

(ii) A cure reaction of low enthalpy took place in the sample, following the heating process. This case was more complicated than the first one, because of the superimposition of two heat transfers, one due to heat conduction and the other due to the exothermic reaction. In this case, the temperature gradients provoked by the reaction were substantially lower than those due to heat conduction, and various laws could be derived for describing the process [7,8].

(iii) In the case of a reaction of high enthalpy, such as that which occurred in thermosets (50–100 cal g^{-1}), the problem became extremely complicated because of the superimposition of the temperature gradients indicated in (ii). A first approach was made in the case of large samples (100 mg) by considering reactions with various values of enthalpy ranging from 15 to 75 cal g^{-1} [4].

The purpose of this work was to study the high enthalpy (76 cal g^{-1}) cure process of epoxy resin and to observe the effect of the sample size on the heat flux–temperature histories obtained in DSC. At the same time, other additional information such as the temperature profiles and the state of cure developing through the sample were examined. These studies were conducted with the help of a model built by using a numerical method with finite differences. This model took into account not only the heat transferred by conduction through the sample [9] but also the heat evolved from the cure reaction. Two samples, both cylindrical in shape, were considered, one with a diameter of 0.5 cm (100 mg) and the other with a diameter of 0.2 cm.

In both cases, radial heat conduction was assumed to take place, and the quality of contact between the calorimeter and sample was assumed to be perfect. As no measurement was possible for the determination of the temperature gradients, the validity of the model was tested by comparing the experimental and calculated heat flux obtained with the larger samples (0.5 cm diameter).

THEORETICAL

In order to investigate the effect of the size of the sample on the process taking place within the sample in the calorimeter, the following conditions applied:

(i) Cylindrical samples of various sizes were studied.

(ii) Only the radial heat conduction through the circular cross-section of the sample was considered, the length of the cylinders being very long compared with their radii.

(iii) The temperature of the surface of the holder and material was equal to the temperature of the calorimeter oven, the thermal contact between sample and calorimeter being perfect.

(iv) Thermal properties, e.g. thermal conductivity and heat diffusivity were taken to be constant.

(v) The kinetics of the cure reaction in resin were described by a single reaction with a constant energy of activation and a constant order of reaction.

(vi) The state of cure (SOC) in the resin at time t was expressed as the enthalpy evolved from the reaction up to time t as a fraction of the total enthalpy.

Mathematical treatment

The rate of temperature rise in the cylindrical sample was given by the equation of heat conduction with superimposition of internal heat generated by the exothermic reaction

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

In DSC experiments (starting with fresh uncured material), the temperatures of the calorimeter and sample were increased at a constant rate from room temperature to the final temperature at which the reaction was complete.

The initial and boundary conditions were as follows

$$t = 0 \qquad 0 \leqslant r \leqslant R \qquad T = T_{\mathrm{ini}} \tag{2}$$

$$t > 0 \qquad r = R \qquad T = T_{\mathrm{ini}} + bt \tag{3}$$

The kinetics of heat generated up to time t by the cure reaction was expressed by the equation

$$\frac{1}{Q_\infty} \frac{\mathrm{d}Q_t}{\mathrm{d}t} = k_0 \left(1 - \frac{Q_t}{Q_\infty} \right)^n \exp\left(- \frac{E}{RT} \right) \tag{4}$$

Numerical analysis

As no analytical solution could be found for eqn.(1), because of the presence of heat generated by the cure reaction (expressed by eqn. (4)), the problem was solved with the help of a numerical method with finite differences.

As shown in Fig. 1, the circular cross-section of the sample was divided into concentric circles of radii $r - \Delta r$, $r + \Delta r$. The heat balance calculated in the ring located between the radii $r - (\Delta r/2)$ and $r + (\Delta r/2)$ enabled us to determine the temperature in the ring at the time $(i + 1)\Delta t$ (denoted TN_r) as

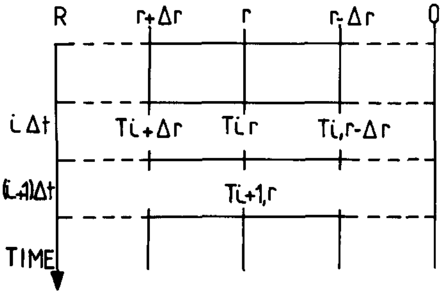

Fig. 1. The temperature–space diagram used for numerical analysis.

a function of the temperature obtained at the preceding time in the same ring and the two adjacent rings.

$$\mathrm{TN}_r = \frac{1}{M}\left[T_{r+\Delta r} + (M-2)T_r + T_{r-\Delta r}\right] + \frac{\Delta r}{2rM}\left[T_{r+\Delta r} - T_{r-\Delta r}\right] + \frac{1}{C}\frac{\mathrm{d}Q}{\mathrm{d}t}\Delta t \tag{5}$$

At the middle of the cross-section ($r = 0$), the following equation was used

$$\mathrm{TN}_0 = \frac{4}{M}\left[T_{\Delta r} - T_0\right] + \frac{1}{C}\frac{\mathrm{d}Q}{\mathrm{d}t}\Delta t + T_0 \tag{6}$$

In both eqns. (5) and (6), the dimensionless number M was expressed in terms of the increments of space Δr and Δt

$$M = \frac{(\Delta r)^2}{\Delta t}\frac{\rho C}{\lambda} \tag{7}$$

To take advantage of the model, the heat flux emitted through the interface between the holder surface and the calorimeter was calculated, as well as the value of the state of cure in the sample.

The heat flux (HF) was proportional to the temperature gradient near the surface of the sample

$$\mathrm{HF} = -\lambda\frac{T_r - T_{r-\Delta r}}{\Delta r} \tag{8}$$

The heat generated by the cure reaction could be calculated with the recurrent relations

$$Q_{i+1} - Q_i = \left(\frac{\mathrm{d}Q}{\mathrm{d}t}\right)_i \Delta t = k_0(Q_\infty - Q_i)^n Q_\infty^{1-n} \exp\left(-\frac{E}{RT}\right) \tag{9}$$

with

$$Q_i = \sum_{j=0}^{i}\left(\frac{\mathrm{d}Q}{\mathrm{d}t}\right)_j \Delta t \text{ and } Q_0 = 0 \tag{10}$$

and the state of cure (SOC) was determined by the ratio

$$\mathrm{SOC}_i = \frac{Q_i}{Q_\infty} \times 100 \tag{11}$$

EXPERIMENTAL

Apparatus

Experiments were carried out using a calorimeter (DSC III, Setaram, Lyon) and a rather large sample. The sample of about 150 mg was located in a stainless steel holder, cylindrical in shape, with an external diameter of about 5.5 mm. The calorimeter detector was in good contact with the holder, so that the temperature of the holder can be assumed to be close to that of the calorimeter block. In fact a thin layer of air exists, with a thickness < 0.1 mm, between the holder and calorimeter. In spite of this, the quality of contact between the holder and calorimeter, which we examined recently [5,6] can be considered as very good, if not perfect.

The heat flux transferred through the holder surface was directly equal to the signal emitted by the calorimeter detector.

Materials

An epoxy resin with two components (epoxy DGEBA and cycloaliphatic hardener) was used in the study. The formulation chosen contained 80 : 100 (w/w) curing agent : resin. The mixture was previously prepared at room temperature by adding the curing agent with vigorous stirring until a clear liquid was obtained.

The kinetics and enthalpy of reaction were determined by using the same calorimeter running in scanning mode at low heating rates (0.5 or 1°C min^{-1}).

The kinetic and thermal parameters were as follows: $Q = 76$ cal g^{-1}, $k_0 = 4 \times 10^{11}$ (s^{-1}), $E = 27140$ (cal mol^{-1}), $\alpha = 10^{-3}$ ($\mathrm{cm}^2\ \mathrm{s}^{-1}$), $n = 1.5$, $\lambda = 10^{-3}$ (cal $\mathrm{cm}^{-1}\ \mathrm{s}^{-1}\ \mathrm{deg}^{-1}$), $C = 0.2 + 0.003 \times T$ (°C) (cal $\mathrm{g}^{-1}\ \mathrm{deg}^{-1}$).

RESULTS

Heat flux–temperature histories were determined by calculation and experiment for the large sample (radius = 0.25 cm) and by calculation for the small sample (radius = 0.1 cm). Other calculations were carried out with

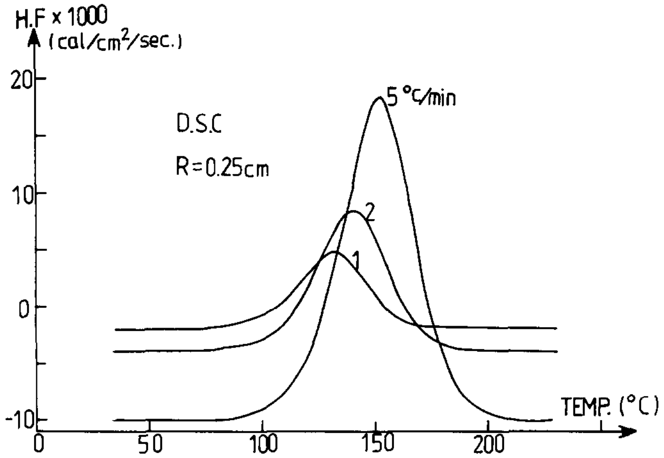

Fig. 2. Heat flux–temperature histories for the large sample (radius = 0.25 cm) at various heating rates (1, 2 and 5 °C min^{-1}).

the help of the model, as the temperature profiles and the state of cure profiles developed within the sample (for the large and small sample).

Heat flux–temperature histories

Heat flux–temperature (or heat flux–time) histories are of interest, because they are directly recorded from the calorimeter running in scanning mode.

These heat flux–temperature histories are shown in Fig. 2 for the large sample (radius = 0.25 cm) and in Fig. 3 for the small sample (radius = 0.1 cm), as they were calculated with the help of the model, for various heating rates ranging from 1 to 5 °C min^{-1}.

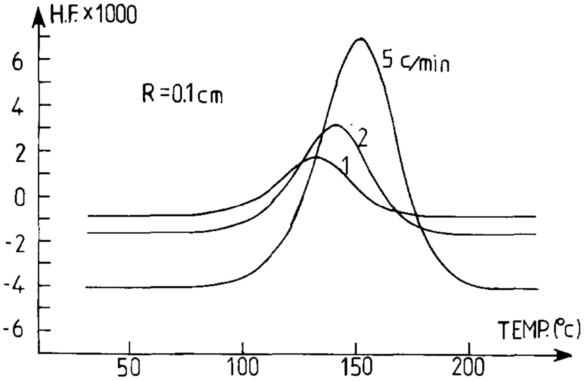

Fig. 3. Heat flux–temperature histories for the small sample (radius = 0.1 cm) at various heating rates (1, 2 and 5 °C min^{-1}).

Some results are worth noting:

(i) The position of the heat flux–temperature peak was found to vary with the heating rate. As shown in a previous paper [4], these peaks were shifted towards a higher temperature when the heating rate was increased.

(ii) The value of the heat flux depended on the values of heating rate and on the dimensions of the sample. The heat flux was found to be proportional to the heating rate as shown previously [4] in both cases: when no reaction occurred, the heat flux was below zero; when the reaction took place in the sample, the heat flux increased and passed through a maximum.

(iii) The effect of sample size was also important. Thus, when no reaction occurred, and when the reaction took place, the heat flux was proportional to the dimension of the sample. In our case, it was 2.5 times higher for the large sample than for the small sample.

(iv) The curves expressing the heat flux as a function of temperature for the large and the small sample were homothetic with regard to the heat flux when they were obtained at the same heating rate. In other words, the curves obtained for the two different samples and calorimeters exhibited a maximum at the same temperature.

Temperature profiles–temperature histories

The temperature difference calculated between the middle and the face of the sample as a function of the temperature of the calorimeter for various values of the heating rate, are shown in Fig. 4 (the large sample) and Fig. 5

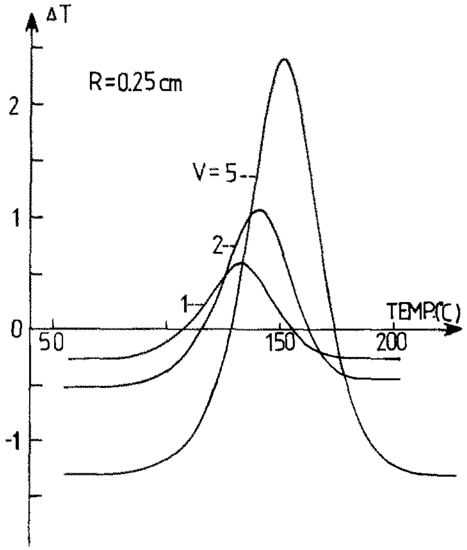

Fig. 4. Temperature difference between the middle and the face of the large sample (radius = 0.25 cm) as a function of temperature, for various heating rates (1, 2 and 5 °C $\min^{-1}$).

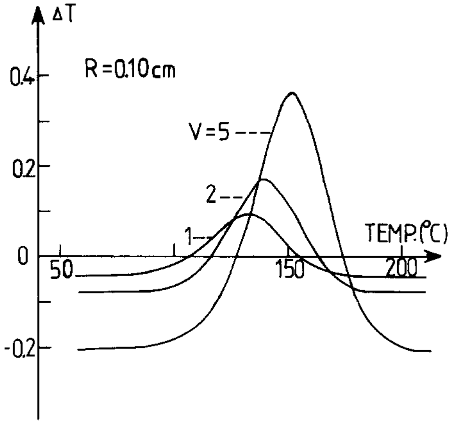

Fig. 5. Temperature difference between the middle and the face of the small sample (radius = 0.1 cm) as a function of temperature, for various heating rates (1, 2 and 5 °C min^{-1}).

(the small sample). The following conclusions can be drawn from these figures:

(i) A good agreement was observed between these curves and the heat flux–temperature histories, the heat flux resulting from the presence of temperature gradients through the sample and near its surface.

(ii) The temperature was found to be higher on the face than at the middle of the sample, when no reaction occurred. This difference was due to the time necessary for heat to be transferred through the sample [4]. This difference in temperature was proportional either to the heating rate of the calorimeter or to the square of the dimension of the sample (e.g. the radius).

(iii) When the reaction took place, the temperature at the middle of the sample increased because of the exothermic cure reaction. As a result, the curves shown in Fig. 4 and Fig. 5 exhibited a maximum. This maximum for the difference in temperature was at the same position along the temperature axis whatever the size of the sample when the heating rate was the same.

TABLE 1

Effect of the radius on heat flux and ΔT

Radius (cm)	Heating rate (°C min^{-1})	$\Delta T/R^2$ Min	$\Delta T/R^2$ Max	HF/R Min	HF/R Max
0.1	1	−4	13	−8.1	26.4
0.1	2	−8	25	−16.2	48.9
0.1	5	−21	57	−40.6	110.3
0.25	1	−4.1	13.7	−8.1	26.5
0.25	2	−8.3	25.4	−16.2	49.5
0.25	5	−20.8	59.4	−40.6	113.7

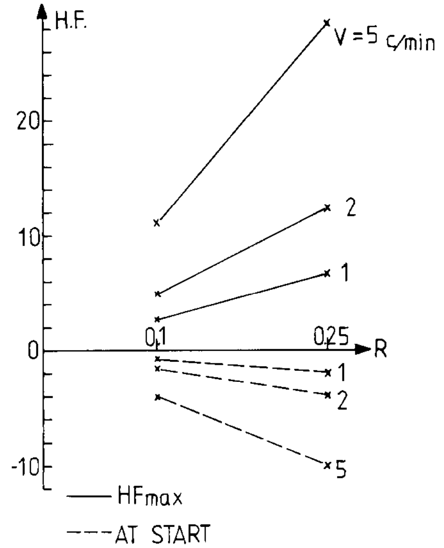

Fig. 6. Heat flux as a function of radius of the sample for various heating rates (see text).

These results described above are expressed in Table 1, where the values of the ratios $\Delta T/R^2$ and $\Delta \mathrm{HF}/R$ are shown for various heating rates.

The values corresponding to the minimum were obtained when no reaction occurred and the values denoted as maximum were obtained at the maximum heat flux.

The values of ΔT were also plotted as a function of the heating rate in various cases (when no reaction occurs, at the maximum heat flux, and when

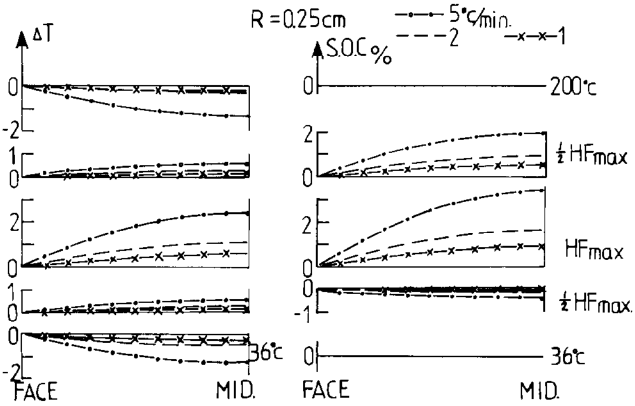

Fig. 7. Profiles of temperature (left) and state of cure (right) developed through the large sample (radius 0.25 cm) at various heating rates (1, 2 and 5 ° C min^{-1}).

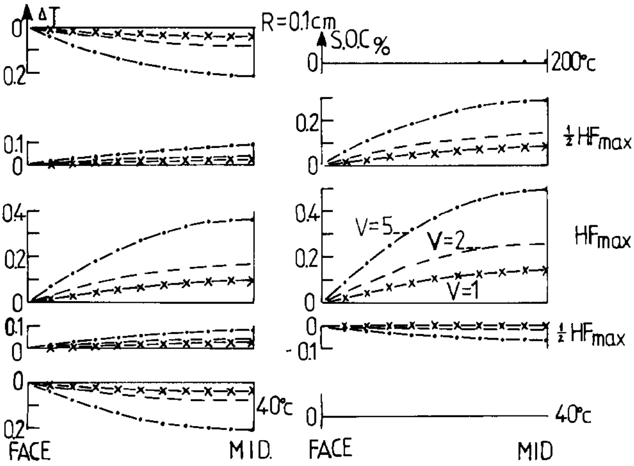

Fig. 8. Profiles of temperature (left) and state of cure (right) developed through the small sample (radius 0.1 cm) at various heating rates (1, 2 and 5 °C $\min^{-1}$).

the heat flux is half the maximum value) for the two samples. As shown in Fig. 6, straight lines were obtained, showing that ΔT is proportional to the heating rate.

Temperature profiles and state of cure through the sample

The temperature profiles and state of cure along the radius of the sample are shown at various times, for various values of the heating rate for the large sample (Fig. 7) and for the small sample (Fig. 8). The effect of the size of sample can be clearly appreciated by comparing the curves in the two figures. The following conclusions can be drawn:

(i) For both samples, the temperature difference ΔT was found to be proportional to the square of the dimension of the sample at any time, at the same heating rate.

(ii) The difference between the state of cure obtained at the middle and on the face of the sample (denoted ΔSOC) was also proportional to the square of the dimension of the sample.

CONCLUSIONS

Following other fundamental research on the effect of parameters on the curves obtained in a calorimeter running in scanning mode, we examined the effect of the dimension of the sample. In order to make comparisons clearer and simpler, two cylindrical samples of different radii were studied.

Some results of interest were found for the heat flux–temperature histories and for the temperature profile developed through the sample.

For the two samples, the heat flux–temperature histories were found to be similar with respect to the heat flux axis, the ratio of similarity being equal to the ratio of the dimensions of the samples. Therefore the position of the heat flux maximum corresponding with the reaction rate maximum was obtained at the same calorimeter temperature.

Likewise, the temperature difference–temperature histories obtained under the same conditions of heating rate in the two samples, were found to be similar. However, the ratio of similarity in this case was proportional to the square of the ratio of the dimensions of the samples. Moreover, the heat flux and temperature difference histories were the same as far as the temperature axis was concerned.

Some state of cure gradients were also developed through the sample in the same way as for the temperature. These state of cure gradients were found to be proportional to the square of the dimension of the sample.

It can be seen that sample size plays an important role in calorimetry. On the one hand, studies on polymer mixtures use quite large samples because of the heterogeneity of the material. On the other hand, an increase in the size of the sample leads to an increase in the heat flux and an increase in the temperature gradients developed through the sample.

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