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EFFECT OF THE ENTHALPY, SAMPLE SIZE AND HEATING RATE ON THE CURE REACTION OF RUBBER IN DSC

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ABSTRACT

As a continuation of the recent studies devoted to the determination of profiles of temperature and state of cure developed through the sample when heated in a calorimeter working in scanning mode, the effect of the enthalpy of reaction, of rather low value, on these profiles was investigated. The effect of the cure enthalpy on the heat flux emitted through the sample–calorimeter interface was especially studied, for various heating rates and various sample sizes. Moreover, the effect of a change of this cure enthalpy on the heat flux and profiles of temperatures and state of cure was determined and reported. These results were obtained not only by experiments in case of the size of the sample available for our calorimeter, but also by calculation with the help of a numerical method with finite differences. This model took into account heat transferred by conduction and the heat generated by the cure reaction.

INTRODUCTION

The role of heat transfer is of primary importance in many industrial reactions as it is frequently the most significant limiting factor in the efficiency of a process and, therefore, has considerable impact on the thermodynamic and kinetic aspects of any chemical engineering involved. However, on a smaller scale, in laboratory applications of thermal processes and the study of their effects, it appeared that the importance of heat transfer was less critical, at least when the value of the heating rate was not considered.

When a sample, at ambient temperature, is placed in an isothermally heated oven, conduction within the specimen is first in a transient condition and, over a finite time, the steady state is eventually reached [1,2]. On the other hand, if the material is heated in the scanning mode by conduction, heat is transferred under transient conditions during the whole term of the process and, consequently, very large temperature gradients can be established not only across the calorimeter–material interface but also within the specimen [3,4]. These gradients of temperature, as well as the heat flux emitted through the calorimeter–sample interface, depend largely on the value chosen for the heating rate of the oven. The influence of sample size is also of great relevance; how representative is a small sample (1–5 mg) taken from a large batch, particularly when that batch contains a number of ingredients which are purportedly homogeneously dispersed? Larger samples (100–200 mg), subjected to high heating rates can easily develop untimely temperature gradients within the mass due to the low thermal conductivity of the material and to the internal heat evolved from the chemical reaction.

Recently, the situation has been clarified in that the effects of heating rate and sample size on various factors in DSC have been rigorously studied, ordered and quantified in terms of heat flux, by considering the two different cases: (i) no reaction takes place in the sample [5]; (ii) a cure reaction of low enthalpy takes place in the sample, following the heat process. The second case is more complicated than the first one, because of the superimposition of two heat transfers, one due to heat convection and the other due to the chemical reaction. However, when the enthalpy of reaction is rather low (5 cal g^{-1}), the gradients of temperature provoked by the chemical reaction are lower than those due to heat convection, so that various laws can be obtained for describing the process. However, in the case of a reaction with high enthalpy, such as that which occurs in thermosets (50–150 cal g^{-1}), the problem becomes extremely complicated and it is unfeasible at the present time.

In the framework of a large study concerned with the heating rate and sample size in DSC for a large range of enthalpy of reaction, a preliminary work was necessary to determine the effect of a slight variation in the enthalpy, when this enthalpy is low. The purpose of this paper was devoted to the study of the cure of rubber in DSC, when its enthalpy was in the range 4–6 cal g^{-1}. The effect of this variation in the cure enthalpy on the profiles of temperature and state of cure developed within the sample was particularly studied by using various values for the heating rate and sample size.

THEORETICAL

In order to simplify the problem, the following assumptions were made.

(i) The radial heat conduction only was considered through the circular cross-section because the length of the cylinder is very long compared to the radius.

(ii) The thermal properties (thermal conductivity, heat capacity) were constant during heating and reaction.

(iii) The temperature of the holder was considered to be equal to the temperature of the rubber-holder interface and to that of the oven.

(iv) The state of cure (SOC) of the rubber was expressed by the ratio of the heat evolved from the cure reaction at time t and the total heat of reaction. The kinetics of the heat of cure reaction were determined by calorimetry.

(v) The enthalpy of cure was supposed to be proportional to the percentage of sulfur in the rubber.

Mathematical treatment

The classical equation for heat conduction through the circular cross-section could be used for the present problem because of the above assumption (ii) for the constancy of thermal properties; i.e.

$$\rho C\frac{\partial T}{\partial t} = \lambda\frac{\partial^2 T}{\partial r^2} + \rho\frac{\mathrm{d}Q}{\mathrm{d}t} \tag{1}$$

where ρ is the density of the material, C is the heat capacity, T is temperature, t is time, r is the radius, Q is the heat of cure evolved, and λ is the thermal conductivity. In the second term of eqn. (1), the contribution of the conduction heat and internal reaction heat for the increase in temperature could be seen.

The constant rate of heating of the calorimeter on the rubber surface was written as follows:

$$T_{t,R} = T_{t-1,R} + b\Delta t \tag{2}$$

where b is a constant. The initial and boundary conditions were:

$$t = 0 \qquad 0 \leqslant r \leqslant R \qquad T_{\text{sample}} \tag{3}$$

$$t > 0 \qquad r > R \qquad T = T_{\text{calorimeter}} \tag{4}$$

$$0 < r < R \qquad T_{\text{sample}}$$

where R is the radius of the sample.

The kinetics of the heat evolved from the cure reaction was expressed in the usual way [1–4]

$$\frac{1}{Q_\infty}\frac{\mathrm{d}Q_t}{\mathrm{d}t} = k_0\left(1 - \frac{Qt}{Q_\infty}\right)^n \exp - \frac{E}{RT} \tag{5}$$

where Q_t is the heat of cure evolved up to time t, Q_∞ is the enthalpy of cure, k_0 is the constant rate, E is the energy of reaction, and n is the order of reaction.

Numerical analysis

As no analytical solution for eqns. (1) and (5) could be found, the problem had to be solved with the help of a numerical method with finite differences. An explicit method was used for this work because it was very convenient for micro-computers.

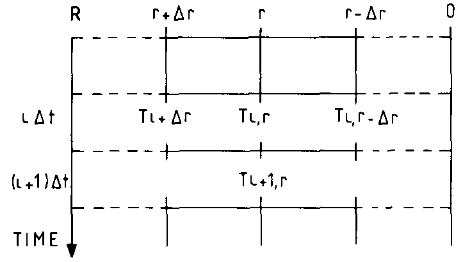

Fig. 1. Scheme of space–time diagram.

The circular cross-section was divided into circles with the following radii, r, $r+\Delta r$, $r+2\Delta r$, etc., as shown in Fig. 1. The heat balance determined in the ring located between $r+\Delta r/2$ and $r-\Delta r/2$, allowed the temperature within this ring at the time $(i+1)\Delta t$ to be obtained as a function of the temperature at the preceding time $i\Delta t$:

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

where $M_{i,r}$ is the modulus at time $i\Delta t$ and position r. Equation (6) could not be used to calculate the temperature at the middle of the cross-section because here it is indeterminate. The following equation was found to be convenient for this case:

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

The dimensionless number M shown in both eqns. (6) and (7) was expressed as follows:

$$M=\left[(\Delta r)^2/\Delta t\right](\rho C/\lambda) \tag{8}$$

The heat flux emitted through the calorimeter–holder interface, was equal to that at the holder–rubber interface:

$$HF=\lambda\left[(T_R-T_{R-\Delta r})/\Delta r\right] \tag{9}$$

The heat evolved from the cure reaction was calculated with the following recurrent relation obtained when the order was 1 in eqn. (5)

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

with

$$Q_i=\sum_{i=0}^{i}\left(\frac{\mathrm{d}Q}{\mathrm{d}t}\right)_i\Delta t \tag{11}$$

TABLE 1

Kinetic parameters and thermal properties

Enthalpy: 5 cal g^{-1}	$n=1$	$k_0 = 3 \times 10^9$ s^{-1}
$E = 25{,}400$ cal mol^{-1}	α [a] $= 1.85 \times 10^{-3}$ cm^2 s^{-1}	
$C = 0.49$ cal mol^{-1} deg^{-1}	$\lambda = 9.9 \times 10^{-4}$ cal cm^{-1} deg^{-1} s^{-1}	

[a] α is the thermal diffusivity

and

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

EXPERIMENTAL

Rubber compound

A rubber compound with a cure enthalpy of about 5cal g^{-1} was used. The parameters of the kinetics of the heat evolved from the cure reaction were determined by using a calorimeter (DSC 111-SETARAM) working in scanning mode (see Table 1).

Apparatus

The calorimeter was used in scanning mode by choosing various heating rates ranging from 2 to 20°C min^{-1}. The sample was rather large (100–150 mg), and located in a holder of 0.5 cm diameter.

The heat flux emitted through the oven–holder interface was recorded by a microcomputer (HP 86) coupled to the calorimeter.

RESULTS

In addition to the heating rate and the size of the cylindrical sample, the enthalpy of cure was also especially studied in this paper. As the rubber enthalpy was usually in the range 3–7 cal g^{-1}, we varied the value of the enthalpy by 1 cal g^{-1} around the mean value of 5 cal g^{-1}. The effect of each of these parameters was determined by considering the heat flux and the profiles of temperature and state of cure.

Heat flux obtained at the surface of the sample

Heat flux–time curves were usually obtained by calorimeter measurements, and they were of interest because they were related to the variation of the rate of cure with the temperature in DSC.

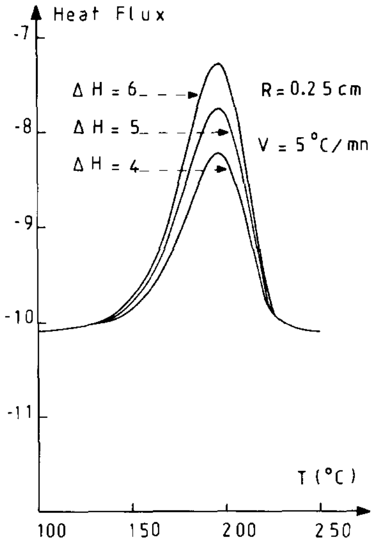

Fig. 2. Heat flux–temperature history for various values of enthalpy (4–6 cal g^{-1}; radius 0.25 cm; 5 °C min^{-1}).

Heat flux–time curves were obtained by calculation with the help of the model, for the following three cases for the three values chosen for the cure

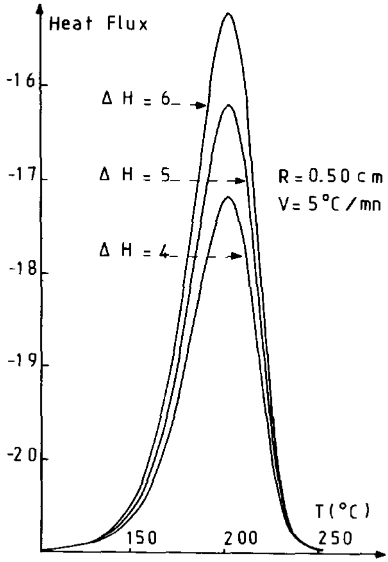

Fig. 3. Heat flux–temperature history for various values of enthalpy (4–6 cal g^{-1}; radius 0.5 cm; 5 °C min^{-1}).

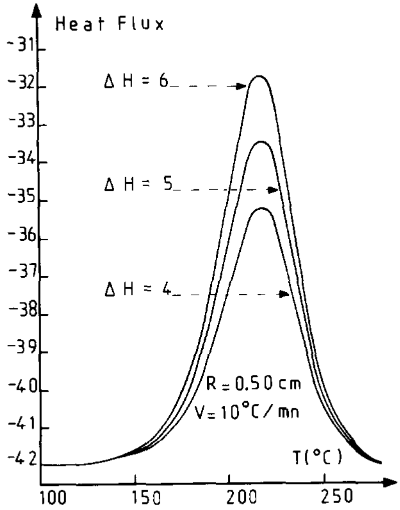

Fig. 4. Heat flux–temperature history for various values of enthalpy (4–6 cal g^{-1}; radius 0.5 cm; 10°C min^{-1}).

enthalpy:

Radius 0.25 cm; heating rate 5°C min^{-1}; Fig. 2.
Radius 0.5 cm; heating rate 5°C min^{-1}; Fig. 3.
Radius 0.5 cm; heating rate 10°C min^{-1}; Fig. 4.

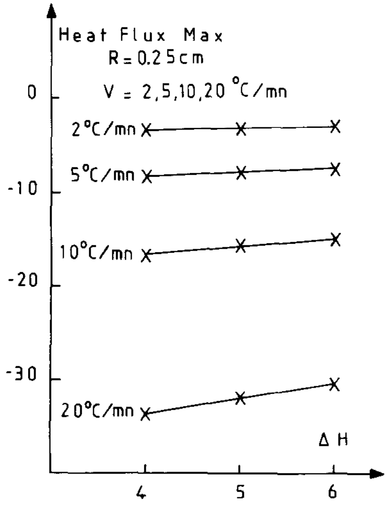

Fig. 5. Maximum of heat flux vs. enthalpy of cure for various heating rates (2–20°C min^{-1}); radius 0.25 cm.

The heat flux–time history obtained for the radius of 0.25 cm and the cure enthalpy of 5 cal g^{-1} was also determined by experiment.

As shown in Figs. 2–4, the maximum values of heat flux rose to the same temperature when the cure enthalpy was varied. Only the sensitivity of the calorimeter, expressed by the value of the heat flux emitted, was found to be proportional to the cure enthalpy as shown in Fig. 5, and to the heating rate.

Profiles of temperature through the sample

Because of the heating of sample under transient conditions in DSC, and because of the internal heat generated by the cure reaction, the temperature of the calorimeter was not that of the sample. Moreover, some profiles of temperature were found to develop through the sample.

Some profiles of the temperature developed within the circular cross-section of the cylindrical sample are shown in Fig. 6 for various values of the cure enthalpy, as obtained by calculation. The temperature was about the same on the surface of the rubber in contact with the holder, but a slight difference in the temperature at the middle of the sample was observed. The temperature–time history at the middle of the sample is shown in Fig. 7 for the various values of enthalpy. These curves (Fig. 7) are similar to the heat flux–temperature curves shown in Fig. 3, the heat flux being proportional to the difference in temperature between the face and the middle of the sample.

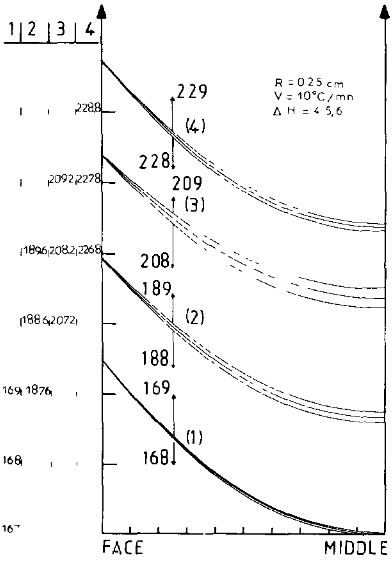

Fig. 6. Profiles of temperature for various enthalpy values and various times (radius 0.25 cm).

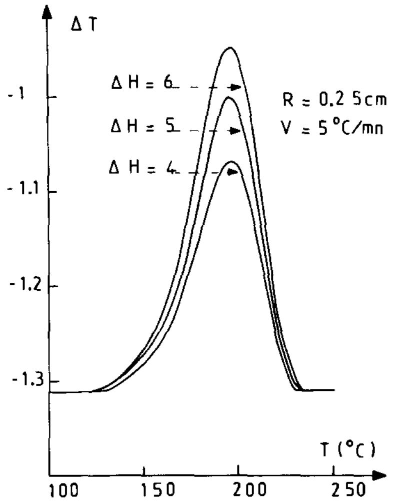

Fig. 7. Difference in temperature (Tmiddle–Tface) vs. temperature for various enthalpies (radius 0.25 cm; 5°C min^{-1}).

State of cure–temperature history

The state of cure–temperature history obtained by calculation is shown in Fig. 8 for a radius of 0.25 cm and a heating rate of 5°C min^{-1}. These curves were very similar, showing little effect of the value of the cure enthalpy on the rate of cure and the state of cure obtained at the middle of the sample, when the enthalpy was varied through the range 4–6 cal g^{-1}.

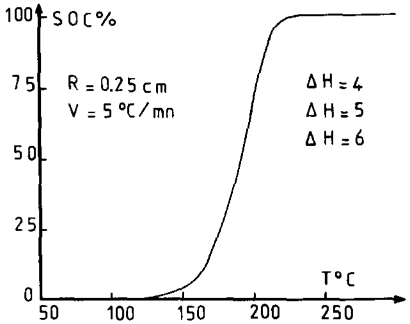

Fig. 8. State of cure–temperature history at the middle of the sample for various values of enthalpy (radius 0.25 cm; 5°C min^{-1}).

CONCLUSIONS

As an extension to our previous works concerned with the determination of the effect of the heating rate and sample size in calorimeter, and especially in DSC measurements, the purpose of this paper was to give new information on the effect of the enthalpy of reaction when this enthalpy was rather low as it is in rubber cure.

The results indicated that the effect of change in the cure enthalpy around the mean value was simple to understand because the value of the enthalpy was low. It was found that heat conducted from the oven of the calorimeter to the sample was of higher importance than the internal heat generated from the cure, so that heat conduction from the oven was mainly responsible for the development of the gradients of temperature in the sample. Thus, in the case of rubber cure, a variation in the cure enthalpy of 1 cal g^{-1} around the mean value of 5 cal g^{-1} was found to provoke a proportional variation in some parameters of interest such as: the heat flux emitted through the sample–calorimeter interface which was usually recorded, and the difference in the temperatures obtained at the middle and the face of the sample. This research is of interest because the experiments showed that cure reactions of rather high enthalpy, as in thermosets, gave quite different results.

LIST OF SYMBOLS

b	rate of heating in calorimeter
C	heat capacity
E	activation energy
k_0	rate constant
$M_{i,r}$	modulus at time $i\Delta t$ and position r
n	reaction order
Q_t	heat of cure evolved up to time t
Q_∞	enthalpy of cure
r	radius
R	radius of the sample
Δt	increment of time
$T_{i,r}$	temperature at time $i\Delta t$ and position r
Δx	increment of space

Greek letters

α	thermal diffusivity
λ	thermal conductivity
ρ	density of the material

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