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

J.Y. ARMAND, J. BOURGOIS, M. TOUCHARD and J.M. VERGNAUD

*Laboratory of Materials and Chemical Engineering, U.E.R. of Sciences,
University of St. Etienne, 23 Dr. P. Michelon, St. Etienne 42100 (France)*

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ABSTRACT

The effect of the heating rate and sample size on the cure reaction of rubber with a low enthalpy (5 cal g^{-1}) is studied in this paper. A numerical method with finite differences, taking into account the heat transferred by conduction through the sample and the kinetics of the heat evolved from the cure reaction, is used with success. Several results are obtained: the heat flux emitted from the sample, the profiles of temperature developed through the sample as well as the state of cure. The problem is complex because two kinds of heat transfer are superimposed, one resulting from the scanning mode and the other with the heat of reaction. For samples of radius lower than 0.25 cm, the heat flux and profiles of temperature due to cure reaction are obtained at the same time. The state of cure–temperature curves determined at the middle of the sample are the same for various samples whose radii range from 0.25 to 1 cm.

INTRODUCTION

When industrial processes are operated in a discontinuous way, in batch processing, as for reactions conducted in moulds, the following steps can be distinguished [1–6]:

(i) The first step is nearly always the heating of the material, by conduction for materials pressed into the slabs of the mould or in the holder of the calorimeter, or also by convection and conduction for materials submitted to pyrolysis. During this step, some temperature profiles are often developed through the sample because of the low heat conductivity of the material.

(ii) The second step is the reaction with its own kinetics and enthalpy; Following the gradients of temperature obtained before, the rate of the reaction varies through the sample instead of being constant as in a reaction conducted under isothermal conditions.

(iii) The exothermicity produced by the reaction (which varies with the rate of the reaction) provokes in turn some temperature gradients which are then responsible for the development of the gradients of state of cure (where rubber is concerned).

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These steps can also be found for the sample heated in the calorimeter on a laboratory scale [7–11].

As a result of these gradients of state of cure obtained in the sample, this heterogeneity in the chemical change may often correspond with another heterogeneity of the material concerned with the mechanical properties. Thus all these facts may explain the presence in the material of internal stresses which are able to develop into cracks.

Whether on a small scale in the calorimeter or in full scale plant with the mould, the same problem is set in order to reduce the time of the reaction cycle. In both these cases, the effect of the heating rate and the size of the sample on the rate at which the reaction is progressing, are of interest. Firstly, studies of this kind can give further insight into the process developed in calorimetry, for which it is desired to reduce the time of experiments by increasing the heating rate and subsequently decreasing the size of the sample. Another application can be found for research aimed at improving the productivity by increasing the size of the sample, when for instance it is desired to predict the operational conditions necessary on a large scale from the results obtained on a laboratory scale.

As an extension of our previous work [12] which was concerned with the effect of the heating rate and sample size on the heat transferred through the sample in the calorimeter when no reaction occurs, the purpose of the present work is to afford a fuller insight into the progress of the heat and advancement of reaction through the sample in the calorimeter when the heating rate and size of sample are varied. Thus the aim of this research is to describe the effect of the heating rate and sample size on the development of the temperature profiles and state of cure through rubber samples heated in a calorimeter working in the scanning mode, when the reaction evolves a low cure enthalpy. Some values are obtained from experiments for one dimension, while others are determined by calculation. These calculations are done by using an explicit numerical method with finite differences, taking into account the heat transferred by conduction and the cure reaction [9–11].

THEORETICAL

The following assumptions are made:

(i) Heat conduction is only radial through the circular cross-section of cylindrical samples.

(ii) The thermal properties of the material, such as thermal conductivity and heat diffusivity, are constant during the heating and reaction.

(iii) The kinetics of the cure of rubber are expressed by the heat evolved from the reaction. The state of cure (SOC) is defined by the ratio of the heat emitted by the reaction at time t and the total heat of reaction.

(iv) The temperature of the holder is the same as that of the oven of the calorimeter.

Mathematical treatment

The equation for radial heat conduction through the circular cross-section is

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

where the contribution of conduction heat and reaction heat are shown, and the increase in temperature of the calorimeter oven is constant

$$\left(\frac{\partial T}{\partial t}\right) = \text{constant} \tag{2}$$

The initial and boundary conditions are

$$t = 0 \qquad 0 \leqslant r \leqslant R_\mathrm{s} \qquad T = T_0 \text{ sample} \tag{3}$$

$$t > 0 \qquad r > R_\mathrm{s} \qquad T = T_\mathrm{m} \text{ calorimeter}$$

$$0 < r < R_\mathrm{s} \qquad T = T_{t,r} \text{ sample} \tag{4}$$

Numerical analysis

There is no analytical solution for eqn. (1), and the problem is solved by an explicit numerical method with finite differences.

By considering the following circles of radius, r, $r + \Delta r$, $r + 2\ \Delta r$, etc., taken on the circular cross-section of the sample, the heat balance can be determined in the ring located between $r + \Delta r/2$ and $r - \Delta r/2$, and the temperature within this ring after the elapse of time Δt can be obtained from the temperatures at the preceeding time.

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

The following equation is suitable for calculating the temperature at the middle, for $r = 0$

$$T_{i+1,0} = \frac{4}{M_{i,0}}\left[T_{i,\Delta r} - T_{i,0}\right] + \frac{1}{C} \cdot \frac{\mathrm{d}Q}{\mathrm{d}t} \cdot \Delta t \tag{6}$$

In both eqns. (5) and (6), the dimensionless number is as follows

$$M = \frac{(\Delta r)^2}{\Delta t} \cdot \frac{1}{\alpha} \tag{7}$$

A simple equation is used for the rubber calorimeter interface [12]

$$T_{i+1,R} = \tfrac{1}{2}\left[T_{i,\mathrm{m}} + T_{i,R}\right] \tag{8}$$

The heat flux transferred through the calorimeter–rubber interface is obtained with the help of the following equation

$$HF = \lambda \cdot \frac{T_R - T_{R-\Delta r}}{\Delta_r} \tag{9}$$

The heat evolved from the cure reaction is expressed by an Arrhenius equation

$$\frac{1}{Q_\infty}\frac{\mathrm{d}Q(r,\,t)}{\mathrm{d}t} = K_0\left(\frac{Q_\infty - Q_{r,t}}{Q_\infty}\right)^n \cdot \exp\left(-\frac{E}{RT}\right) \tag{10}$$

and the cure reaction is calculated with the recurrent relation, when the order n is 1

$$\left(\frac{\mathrm{d}Q}{\mathrm{d}T}\right)_{i+1} \cdot \Delta t = Q_{i+1} - Q_i = (Q_\infty - Q_i)K_0 \cdot \exp - \frac{E}{RT} \tag{11}$$

where $Q_0 = 0$ and $Q_i = \sum_{i=0}^{i}\left(\frac{\mathrm{d}Q}{\mathrm{d}t}\right)_i \cdot \Delta t$.

EXPERIMENTAL

Materials

An industrial rubber compound with an enthalpy of cure of nearly 5 cal g^{-1} is used. The kinetics of the cure reaction are determined by DSC working in the scanning mode with a heating rate of 5°C min^{-1}. This heating rate is chosen by taking into account the low heat flux emitted from the reaction due to the low enthalpy and the low properties of the thermal transport [10]. The parameters for the kinetics of cure reaction and the thermal properties are shown in Table 1.

Apparatus

A differential scanning calorimeter (DSC 111, Setaram) is used in the scanning mode at various heating rates ranging from 2–20°C min^{-1}. About

TABLE 1

Kinetic parameters and thermal properties

Parameter	Value	Parameter	Value
Enthalpy (cal g^{-1})	5	n	1
E (cal mol^{-1})	25.400	K_0 (s^{-1})	3×10^9
C (cal mol^{-1} deg^{-1})	0.49	α (cm^2 s^{-1})	1.85×10^{-3}
		λ (cal cm^{-1} deg^{-1} s^{-1})	9.9×10^{-4}

100 mg of the compound is encapsulated in a hermetically-sealed stainless steel holder.

The apparatus is coupled with a micro-computer (HP 86).

RESULTS

Two parameters are of interest in this work: the heating rate on the cylinder face, and the radius of the cylindrical sample of rubber compound.

Our study is especially concerned with the determination of the efffect of the above two parameters on the evolution of the following data given by calorimetry:

(i) The heat flux emitted through the sample–calorimeter interface due to the exothermal cure reaction of low enthalpy.

(ii) The profiles of temperature developed through the sample during the cure.

(iii) The development of profiles of state of cure (SOC) through the sample during the cure.

Heat flux emitted by calorimeter

These curves are of interest in calorimetry because they are usually determined by experiment. The heat flux–temperature curves are drawn for various sizes of the sample and heating rates, as obtained from experiment with the sample of radius 0.25 cm (Fig. 1), and as calculated with the model for samples of radius 0.5 cm (Fig. 2) and 1 cm (Fig. 3). Various units are used for each of these three samples in order to facilitate their comparison.

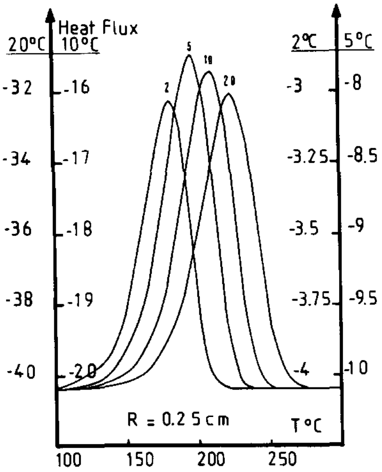

Fig. 1. Heat flux–temperature curves for various heating rates: sample radius, 0.25 cm.

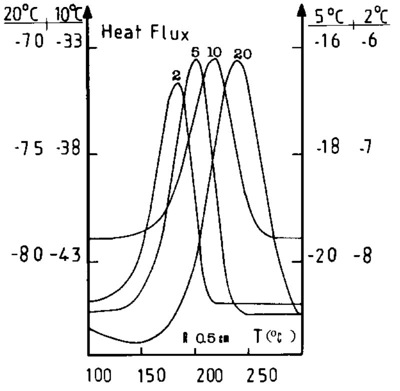

Fig. 2. Heat flux–temperature curves for various heating rates: sample radius, 0.5 cm.

Of course, the baselines corresponding to the heat flux emitted when no reaction occurs are not the same for these various samples heated at different rates [12].

Some results of concern are attained from these heat flux–temperature curves, especially regarding the sensitivity of the technique and the positions of the above curves. The sensitivity of the calorimeter can be expressed by the height of the peak corresponding to the heat flux–temperature curves [10]. As shown in Figs. 4 and 5, the sensitivity is found to be directly proportional to the value of the radius of samples and of the heating rate on the cylindrical sample surface.

Another result of interest is related to the position of the heat flux-temperature peak, and especially the position of the maximum of the peak expressed by the temperature at which it is evolved. The variation of the peak maximum can be appreciated in Fig. 6, as a function of the radius of samples for various heating rates ranging from 2–20 °C min^{-1}. It is not easy

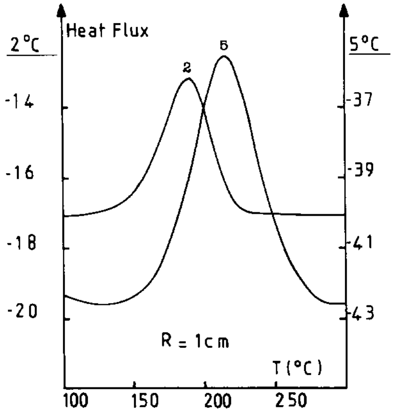

Fig. 3. Heat flux–temperature curves for various heating rates: sample radius, 1 cm.

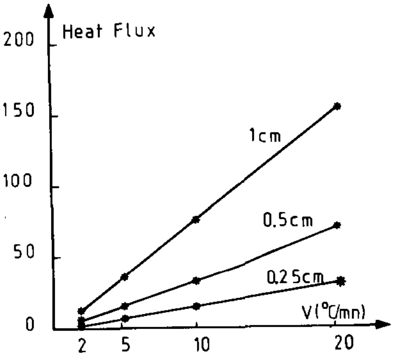

Fig. 4. Heat flux as a function of the heating rate for various sample sizes.

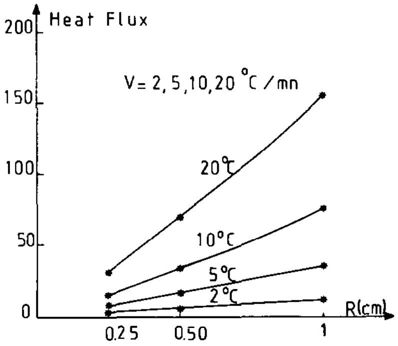

Fig. 5. Heat flux as a function of the radius, for various heating rates.

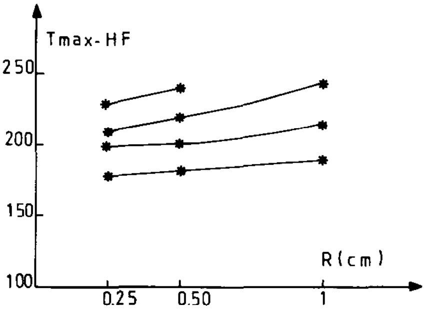

Fig. 6. Position of maximum heat flux (expressed by the temperature at which it is obtained) as a function of the sample radius.

to find a law relating to this above variation. However, it is clear that the larger the radius of samples, the higher the temperature of the maximum heat flux; in the same way, a significant increase in this temperature is shown when higher heating rates are used.

Gradients of temperature within the sample

As shown in previous papers [1,2,11], gradients of temperature are developed within the rubber sample during the curve because of local heating arising from exothermic reactions and low heat transfer through the rubber. Moverover the applied temperature is the set calorimeter temperature and not the rubber temperature during cure, resulting from the total enthalpy of the sample. As the rate of reaction is largely dependent on the temperature, a precise knowledge of the exact temperature within the sample during calorimetry must always be of advantage. In fact the problem is complicated because the heating rate and temperature are connected with each other, the exothermic reaction provoking an increase in temperature and a following increase in the reaction rate and enthalpy change.

Two facts must be considered in turn:

(i) When the material is heated with a constant heating rate on its cylindrical surface, the heat is progressively transferred to the middle, so that the temperature in the middle follows in a retarded way. As a result, the temperature in the middle is always lower than that on the surface when no reaction occurs, this difference being proportional to the square of the radius and proportional to the heating rate [12].

(ii) Following the above fact, the exothermic reaction is responsible for the development of another gradient of temperature within the sample, the temperature being higher at the middle of the sample.

Because the local temperature follows from the superposition of the above two facts, the general problem is complicated, the consequence depending largely on the value of the cure enthalpy.

The difference in the temperatures at the middle and on the surface, as a function of the temperature of the calorimeter are shown in Figs. 7–9 for the

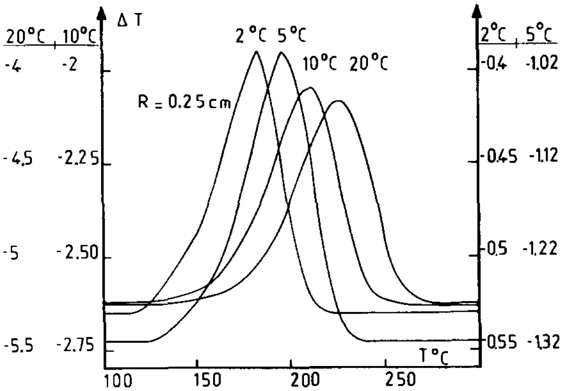

Fig. 7. ΔT ($T_{\mathrm{middle}} - T_{\mathrm{surface}}$) as a function of temperature, for various heating rates: sample radius, 0.25 cm.

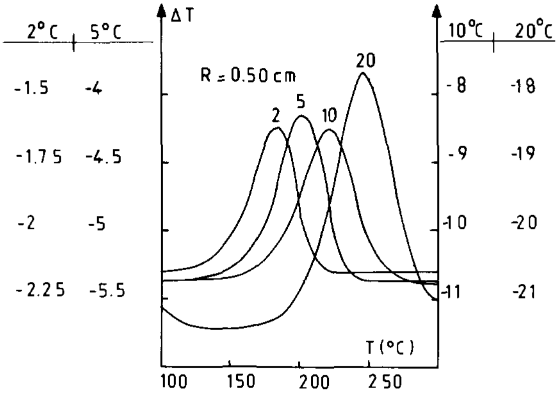

Fig. 8. ΔT ($T_{\text{middle}} - T_{\text{surface}}$) as a function of temperature, for various heating rates: sample radius, 0.5 cm.

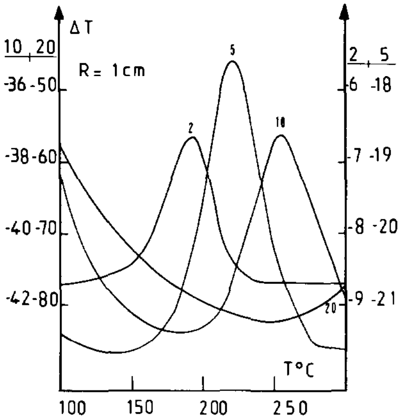

Fig. 9. ΔT ($T_{\text{middle}} - T_{\text{surface}}$) as a function of temperature, for various heating rates: radius, 1 cm.

various sizes chosen for our samples. As an extent of the cure enthalpy, some peaks are obtained, whose heights are approximately proportional to the heating rate and sample size (radius). The point concerned with the position of these peaks is worth attention, and a special table (see below) allows one to give consideration to this value as compared with that obtained with the heat flux.

Profiles of state of cure (SOC) within the sample

As the temperature is not the same in the cross-section of the sample, the rate of cure varies through the sample, and some profiles of SOC must be

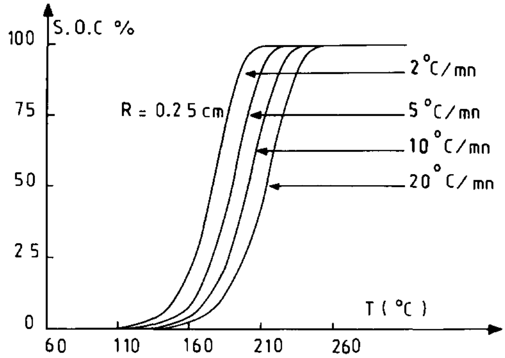

Fig. 10. SOC at the middle vs. temperature, for various heating rates: sample radius, 0.25 cm.

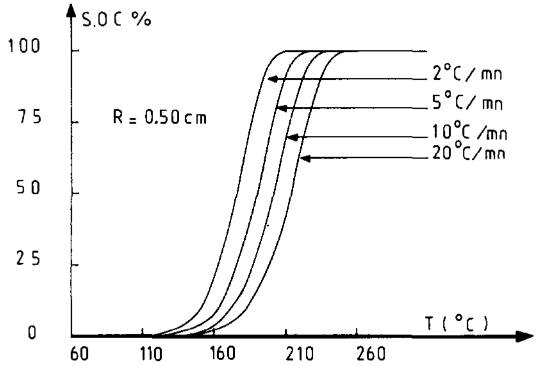

Fig. 11. SOC at the middle vs. temperature, for various heating rates: sample radius, 0.5 cm.

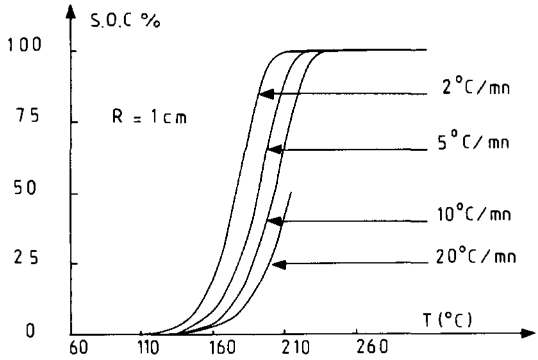

Fig. 12. SOC at the middle vs. temperature, for various heating rates: sample radius, 1 cm.

obtained. These profiles of SOC are shown in Figs. 10–12 for the various sizes of samples, as they were calculated within the help of the model. Of course, the effect of the heating rate is largely dependent on the position of the SOC–temperature curves. So the higher the heating rate, the lower the value of the SOC obtained (at the middle of the sample in the present paper).

By considering the SOC value, and in view of these gradients of SOC within the sample, the rubber is heterogeneous during the cure. There is no doubt that some differences in properties of the final product may be obtained if the temperature–time history of the rubber has been quite different in the various parts of the sample.

DISCUSSION

Various values of the temperature of the middle of the sample, concerned with certain conditions (the maximum of heat flux, HF_{max}; the maximum of the temperature gradients, ΔT_{max}; SOC is 50% at the middle) are shown in Table 2, for various sample sizes and heating rates.

Some facts of interest are worth noticing:

(i) The values of the temperature obtained at the middle when the heat flux and gradients of temperature are maximal, are about the same, especially for the lower sample size at any heating rate. However, when the sample size is increased (for instance when the radius is 1 cm) a difference between these values is apparent which increases with the heating rate.

(ii) The values of the temperature at the middle of samples obtained when the SOC is 50% are about the same for all sample sizes at the same heating rate. In fact, this value varies only with the heating rate.

TABLE 2

Temperatures (°C) of the middle of the sample achieved under different experimental conditions

Sample radius (cm)	Parameter	Heating rate (°C min^{-1})			
		2	5	10	20
0.25	HF_{max}	182.3	197.3	211.3	225.9
	ΔT_{max}	183	197	213	226
	SOC = 50%	176.3	191	201.4	215.5
0.5	HF_{max}	182.8	201.1	217.5	238.2
	ΔT_{max}	185	201	221	246
	SOC = 50%	176.2	190	202	214
1	HF_{max}	189.9	214.1	236	248
	ΔT_{max}	193	221	255	
	SOC = 50%	176.7	191	203.6	215

CONCLUSIONS

Following a previous study [12] concerned with the effect of the heating rate and sample size on the heat transfer through the sample of a calorimeter working in the scanning mode, the aim of this paper has been to determine the effect of these parameters when a reaction occurs in the sample. As the problem is rather complex, resulting from the superposition of two effects (the heat transfer due to the scanning mode and the heat transfer due to the reaction), the study has been achieved by considering a reaction of low enthalpy (the cure of rubber).

Some results are obtained by considering the heat flux emitted through the sample–calorimeter interface, the gradients of temperature developed through the sample and the values of the state of cure at the middle of the sample. The model based on an explicit numerical method with finite differences is able to give this information, by taking into account the kinetics of the heat change evolved from the cure reaction and the heat transferred by conduction through the sample.

In summing up these results, the effect of the sample size and heating rate are superimposed. When the size is of the order of magnitude of our lower sample (radius, 0.25 cm), the heat flux is emitted at about the same time as the gradients of temperature. For larger samples (radius, 1 cm), the problem becomes more complicated, and it is difficult to use heating rates higher than 10°C min^{-1}.

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