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FUNDAMENTAL STUDY OF HEATING PROCESS IN DSC. EFFECT OF THE CURE ENTHALPY AND HEATING RATE

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ABSTRACT

A fundamental study on the process of heating and curing has been performed by considering the sample in the calorimeter whilst running in the scanning mode in order to gain a further insight into the process. The effect of the following two parameters has been especially examined: the heating rate of the calorimeter and the enthalpy of the reaction in the sample. Two different heat transfer processes have been distinguished, although they are superimposed during the process: one is concerned with the sample heating by the calorimeter oven and, the other is due to the presence of internal heat generated by the reaction. The heating rate of the calorimeter plays a role in both these heat transfer methods which are responsible for the development of temperature gradients, these gradients being proportional to the value of the heating rate. The enthalpy of cure only acts on the second heat transfer, and the resulting gradients of temperature are proportional to this enthalpy.

INTRODUCTION

In calorimetry techniques, enthalpy changes accompanying chemical or physical events in the sample are registered as a function of temperature or time. The result obtained is the profile of the rate of enthalpy change either as a function of temperature as the sample is heated at a constant linear rate (differential scanning calorimetry, DSC) or as a function of time when the calorimeter is held at constant temperature (differential calorimetry, DC).

Both these techniques have some advantages and drawbacks, and each of them also have their supporters.

In the DC mode, the calorimeter is stabilized at the desired temperature, and the sample previously at room temperature is introduced. One advantage of the technique is that the enthalpy of the reaction occurring at the constant applied temperature is determined up to a sufficient time. However, the applied temperature is the set calorimeter temperature and not the true sample temperature during reaction because of local heating arising from the exothermic reaction. Moreover, a rather narrow temperature window, e.g., about 20 ° C for accelerated sulfur cure systems [1,2] or for the cure of thermosets [3,4], is found from which meaningful data can be obtained. On the one hand, the lowest temperature for these studies is limitated by the calorimeter sensitivity, the rate of enthalpy change being very low at low temperature. On the other hand, the highest temperature at which experiments can be made, is limitated by the induction period of reaction. Very often this induction period is shorter than the time required for the sample to establish thermal equilibrium in the calorimeter. The first part of the reaction is lost because of the very high temperature gradients developed throughout the sample [5,6]. Because of the presence of these temperature gradients, the high heating period of the sample when it is introduced and also because of the reaction being exothermic the temperature in the sample is not at all well defined as shown in previous studies [5,6]. However an advantage of the DC technique is that the sample is destroyed at a high temperature.

In the DSC experiment, the sample is scanned at a constant heating rate up to a temperature at which the reaction exotherm is complete. The first drawback of the technique is obvious as shown previously: the process is always conducted under transient conditions with a first step necessary for the temperature gradients to be established, followed by a second heating step with a constant temperature gradient [7,8]. The difference in temperature between the face and middle of the sample has been shown to be proportional to the value of the heating rate and to the square of the radius of the sample [9–11]. Another inconvenience of this technique, is that in the DSC, a higher temperature is necessary to complete the cure than in the DC experiment. As a result, this high temperature may be responsible for a degradation of the resin. This fact is especially obvious in case of special rubber with low cure enthalpy: a low heat flux is obtained with a low heating rate, and a thermal degradation is obtained on the face of the sample before the completion of the cure.

In spite of these drawbacks, the DSC technique is widely used, and is much too useful to be taken for granted. However, the problem concerning the temperature gradients developed through the sample remains. This problem is complex because two kinds of temperature gradients are developed in the sample, one being due to the heating rate and the retardation in the heat propagation, and the other due to the exothermicity of the reaction, these gradients being opposite. The effect of parameters such as the heating rate and cure enthalpy on these gradients are of great importance.

The purpose of this paper is to gain a greater insight into the problem of temperature gradients developed through a cylindrical sample. The cure of epoxy resin has been chosen for the exothermic reaction, because of the high value of the cure enthalpy when the resin is pure, and because lower values for the cure enthalpy can easily be obtained by dispersing a non-reactive material into the resin. This study, necessitating a good knowledge of the temperature profiles, has been conducted with the help of a model built by using a numerical method with finite differences. This model takes into account not only the heat evolved from the cure reaction, but also the heat transferred by conduction through the sample. As no measurement is possible for the determination of the temperature gradients, the validity of the model has been tested by comparing the experimental and calculated heat flux [6–8,12].

THEORETICAL

Assumptions

(i) Heat is transferred through the sample by conduction.
(ii) With the sample being cylindrical in shape, only the radial heat through the circular cross-section is considered.
(iii) The kinetics of the heat evolved from the cure reaction is expressed by a classical equation.
(iv) The enthalpy of cure is proportional to the weight per cent of resin.
(v) The thermal properties of the diluting material are about the same as those of the resin.

Mathematical treatment

The increase in temperature is described by the classical equation of transient heat transfer where the contributions due to heat conduction and the internal heat generated by the reaction are taken into account.

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

In contrast to some workers who have used equations with two constant rates and energy of activation [3,4,13], we have expressed the heat evolved from the reaction by the following equation with only one energy of activation [14].

$$\frac{1}{Q_\infty} \frac{\mathrm{d}Qt}{\mathrm{d}t} = k_0 \left(1 - \frac{Qt}{Q_\infty} \right)^n \exp\left(-\frac{E}{RT} \right) \tag{2}$$

In the circular cross-section, the initial and boundary conditions are

$t = 0 \quad 0 \leqslant r \leqslant R_s \quad T = T_r$ sample (3)
$t > 0 \quad r > R_s \quad T = T_m$ calorimeter (4)
$0 \leqslant r \leqslant R_s \quad T = T_{r,t}$ sample

Numerical analysis

As no analytical solution can be found for eqns. (1) and (2) because of the internal heat generated from the cure reaction, the problem has been solved by using a numerical method with finite differences.

By considering the various annuli of radius r, $r+\Delta r$, $r+2\Delta r$, etc..., the heat balance determined within the ring between $r-(\Delta r/2)$ and $r+(\Delta r/2)$ gives

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

where $T_{i+1,r}$ is the temperature of the ring of radius r and thickness Δr, at the time $(i+1)\Delta t$.

Equation (5) is not available for the middle of the sample. The following equation has been obtained from heat balance data for calculating the temperature at the middle of the sample (circle of radius $\Delta r/2$).

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

The dimensionless number shown in eqns. (5) and (6) is as follows

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

where Δr and Δt are the increments of space and time.

The heat flux transferred through the calorimeter–sample interface is obtained by eqn. (8)

$$HF=\lambda_s\frac{T_{Rs}-T_{Rs-\Delta r}}{\Delta r} \tag{8}$$

The heat evolved from the cure reaction is determined by the recurrent relation

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

with

$$Q_0=0 \qquad \text{and} \qquad Q_i=\sum_{j=0}^{j-1}\left(\frac{\mathrm{d}Q}{\mathrm{d}t}\right)_j\Delta t \tag{10}$$

EXPERIMENTAL

Calorimeter

The sample (approx. 150 mg) is put in an aluminium holder. This holder is cylindrical in shape with an external diameter of 6 mm. A heat flux detector is in contact with the holder so that the temperature of the holder face is as close as possible to that of the bloc. The signal emitted by the heat flux detector is directly proportional to the heat transferred through the holder surface per unit time.

The DSC 111 (Setaram) was used for the work, but the results obtained are of interest for any other apparatus if the dimensions and size of the holder are taken into account.

Materials

An epoxy resin with two components: epoxy DGEBA (Lopox 200 ST01) and hardener (cyclo-aliphatic, D 2605) is used in this study. The formulation chosen contains 80 : 100 (w/w) curing agent/resin. The epoxy-hardener mixture is prepared at room temperature by adding the curing agent with continuous stirring until a clear mixture is obtained. Grains of sand are continuously added to the epoxy mixture at room temperature with appropriate stirring [15]. The compositions have been determined experimentally in order to obtain the desired values of enthalpy of cure ranging from 15 to 75 cal g^{-1}. The values of kinetic and thermal parameters are as follows [14]: $\Delta H = 15$, 25, 50 and 75 cal g^{-1}; $k_0 = 4.10^{11}$ s^{-1}; $E = 27140$ cal mol^{-1}; $\lambda = 10^{-3}$ cal cm^{-1} deg s; $C = 0.50$ cal g^{-1} deg; $\rho = 2$; $n = 1.5$.

Calculation

Calculations are made using the model and ten cylindrical slices. The parameters used for calculation were: $H = 24$; $M = 5$; $\Delta r = 0.025$ cm; $\Delta t = 0.125$ s.

RESULTS

It is rather difficult to set conditions for sowing the problem concerning the cure reaction and heat transfer taking place in the sample when it is scanned at a constant heating rate in a calorimeter. Various parameters such as the enthalpy of cure, kinetic and thermal characteristics and the heating rate of calorimetry, are of importance to the process.

For this reason, the problem was simplified in a previous paper [9], in which heat transfer in the calorimeter was only considered as a function of heating rate and sample size. As no reaction occurred in this case, the profiles of temperature developed within the sample working in the scanning mode could be defined as a function of the size of the sample and of the value given to heating rates. The main results obtained in this study was that the process in this case is conducted in transient conditions, with two steps as follows: the first one being when the temperature gradient is developed along the radius of the cylindrical sample from zero at the beginning of the heating stage to a constant value, the second stage having a constant temperature gradient while the temperatures on the face and in various places in the sample are increased at the same rate as the heating rate of the calorimeter. Another result of interest was that the maximum value obtained for the temperature differences between the face and middle of the sample is directly proportional to the heating rate of the calorimeter and to the square of the radius of the sample.

As the enthalpy of cure is the principal parameter studied in this paper, we have determined the effect of this enthalpy on the following occurrences.

(i) The heat flux–temperature history for various enthalpies as well as the relation between the maximum value of heat flux and the enthalpy for various heating rates.

(ii) The difference between the temperature on the face and at the middle as a function of the temperature of the calorimeter for various enthalpies.

(iii) The profiles of temperature and state of cure developed at various times in the sample as a function of the value of the enthalpy.

Heat flux–temperature history

The heat flux–temperature history is determined for various heating rates ranging from 0.5 to 5°C min^{-1} and for the following values given to the

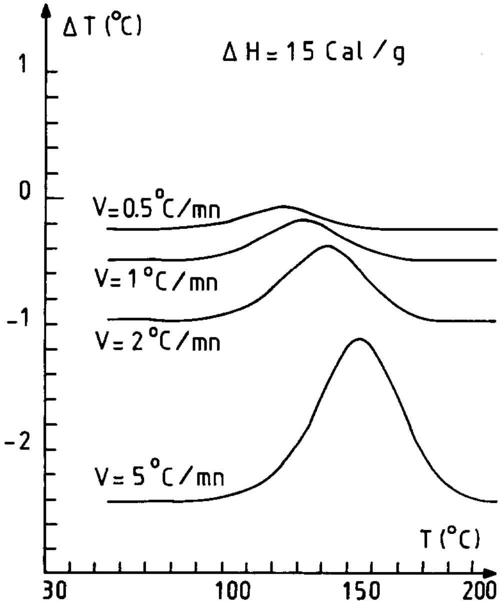

Fig. 1. Heat flux–temperature history for various heating rates ranging from 0.5 to 5°C min^{-1}. Cure enthalpy = 15 cal g^{-1}.

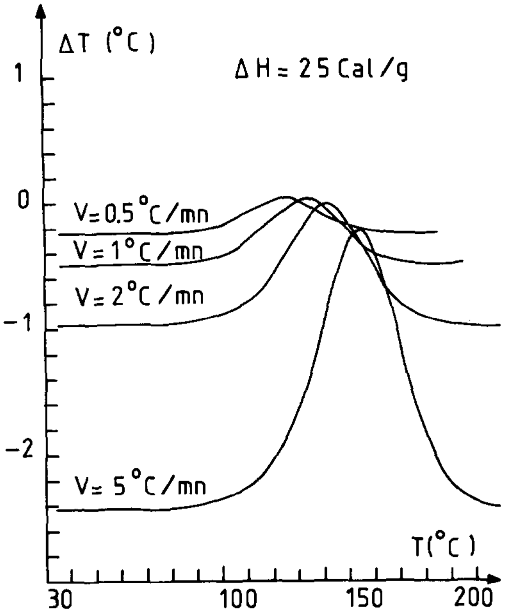

Fig. 2. Heat flux–temperature history for various heating rates ranging from 0.5 to 5 °C min^{-1}. Cure enthalpy = 25 cal g^{-1}.

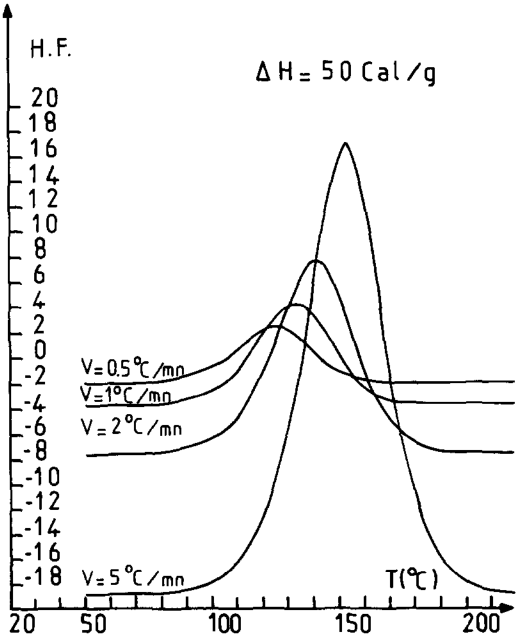

Fig. 3. Heat flux–temperature history for various heating rates ranging from 0.5 to 5 °C min^{-1}. Cure enthalpy = 50 cal g^{-1}.

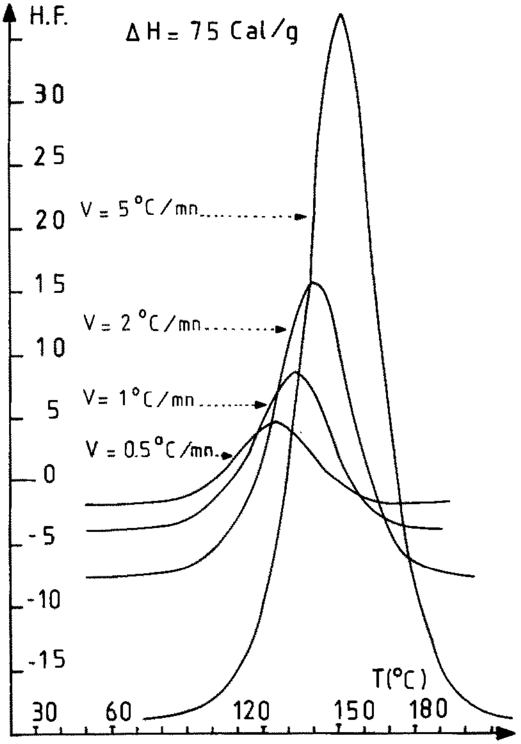

Fig. 4. Heat flux–temperature history for various heating rates ranging from 0.5 to 5°C $\min^{-1}$. Cure enthalpy = 75 cal g^{-1}.

enthalpy of cure: 15, 25, 50 and 75 cal g^{-1} (Figs. 1–4). As shown in these figures, these two parameters have a marked effect on the heat flux–temperature curves.

The heating rate of the calorimeter has the following effects on these curves.

(i) The height of heat flux–temperature peaks depends largely on the heating rate. As shown recently, the sensitivity of the calorimeter expressed by the value of the heat flux is directly proportional to the heating rate [10].

(ii) Another result of interest is related to the position of the heat flux–temperature peak, and especially the position of the maximum of this peak. This position, defined by the temperature of the calorimeter at which the maximum of the heat flux is obtained, is stated as a function of the value of heating rate, as shown in Fig. 5. The heat flux–temperature peaks are shifted towards the higher temperature when the heating rate is increased, essentially because the true temperature of the sample is not the calorimeter temperature, and because the rate of heat transfer through the sample is a limiting factor, being lower than the rate of increase in temperature in the calorimeter and on the face of the sample.

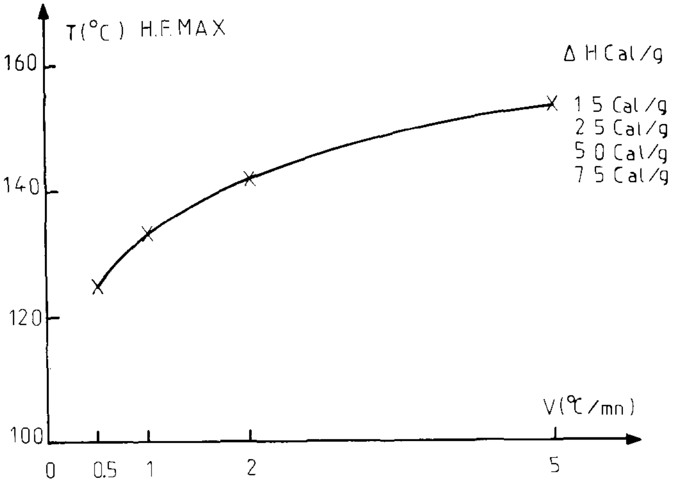

Fig. 5. Variation of the position of the maximum of heat flux as a function of the heating rate for various cure enthalpies.

(iii) The position of the heat flux–temperature peaks along the heat flux axis is also dependent on the value of the heating rate of the calorimeter. This fact is due to a temperature difference between the face and the middle

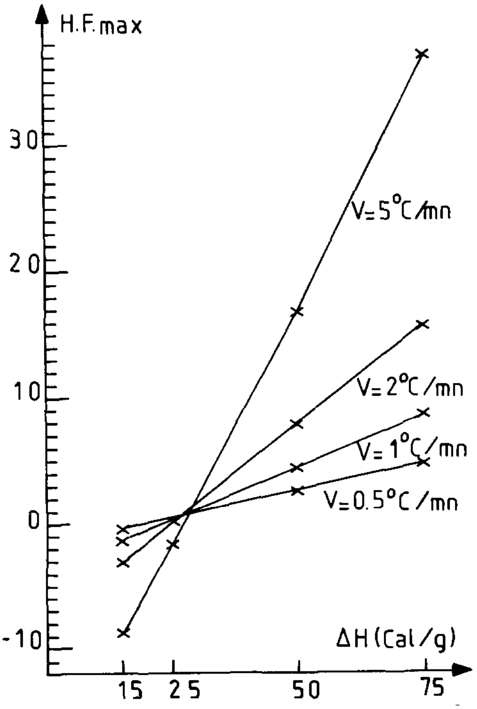

Fig. 6. Maximum heat flux as a function of the cure enthalpy for various heating rates.

of the sample, because of the time taken for the heat to progress through the sample. This difference was found to be directly proportional to the value of the heating rate [9].

The role played by the enthalpy of cure on the heat flux–temperature histories is clearly illustrated in the various figures (Figs. 1–4) obtained for different values of the enthalpy, as well as in Fig. 6 where the maximum value of the heat flux is plotted as a function of the enthalpy for various values of the heating rate. The effect of the enthalpy of cure can be defined by the following points:

(i) Of course, the heat flux is increased with increasing enthalpy, with a constant factor of proportionality as proved in Fig. 6, concerned with the maximum value of the heat flux.

(ii) A linear relationship obtained between the maximum heat flux value and the enthalpy is found for various values of the heating rate, the slope of these straight lines being proportional to the value of the heating rate (Fig. 6).

(iii) As a result, the position of the heat flux–temperature curves along the heat flux axis is largely dependent on the value of the enthalpy. As shown in Figs. 1–4, and especially in Fig. 6, the heating process taking place may be either endothermic or exothermic for the sample according to the values of the enthalpy and heating rate.

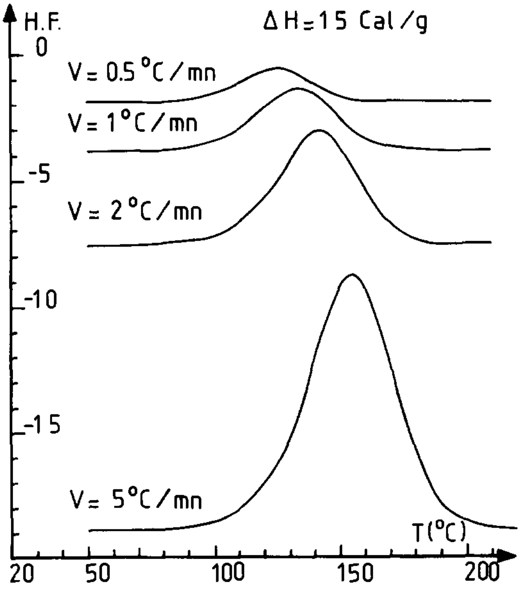

Fig. 7. Difference in temperatures from the middle to the face of the sample as a function of the temperature of the calorimeter for various values of the heating rate. Cure enthalpy = 15 cal g^{-1}.

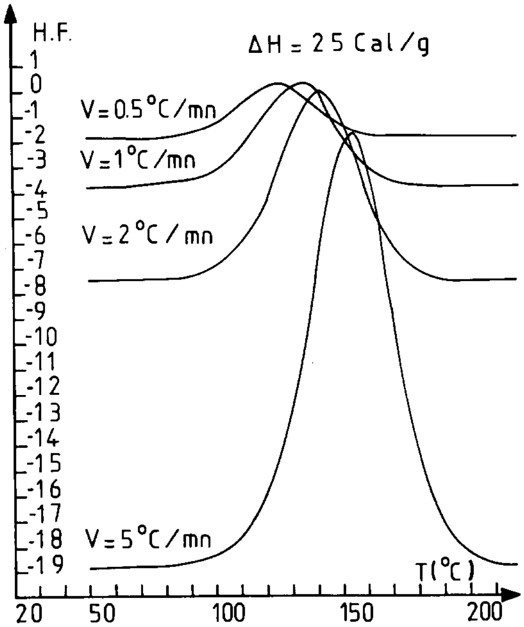

Fig. 8. Difference in temperatures from the middle to the face of the sample as a function of the temperature of the calorimeter, for various values of the heating rate. Cure enthalpy = 25 cal g^{-1}.

Effect of cure enthalpy on the difference of temperatures at the middle and on the face of the sample

The temperature difference calculated at the middle and on the face of the sample are drawn as a function of the temperature of the calorimeter for

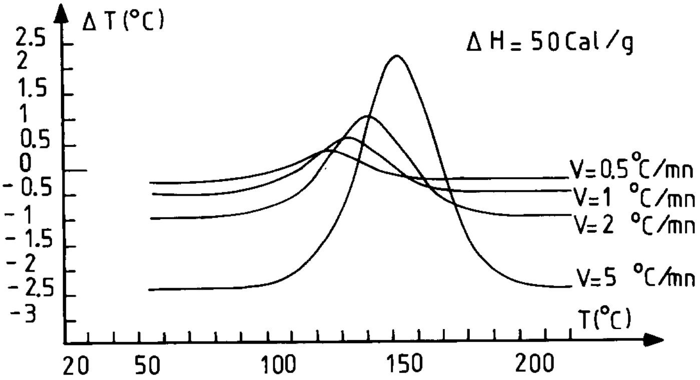

Fig. 9. Difference in temperatures from the middle to the face of the sample as a function of the temperature of the calorimeter for various values of the heating rate. Cure enthalpy = 50 cal g^{-1}.

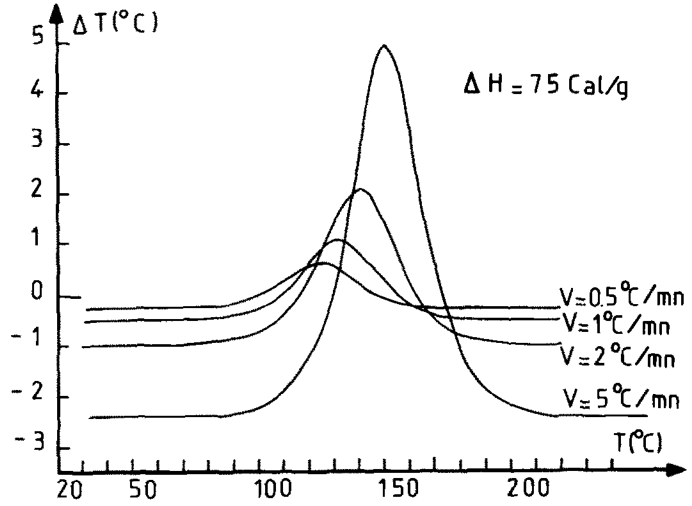

Fig. 10. Difference in temperatures from the middle to the face of the sample as a function of the temperature of the calorimeter for various values of the heating rate. Cure enthalpy = 75 cal g^{-1}.

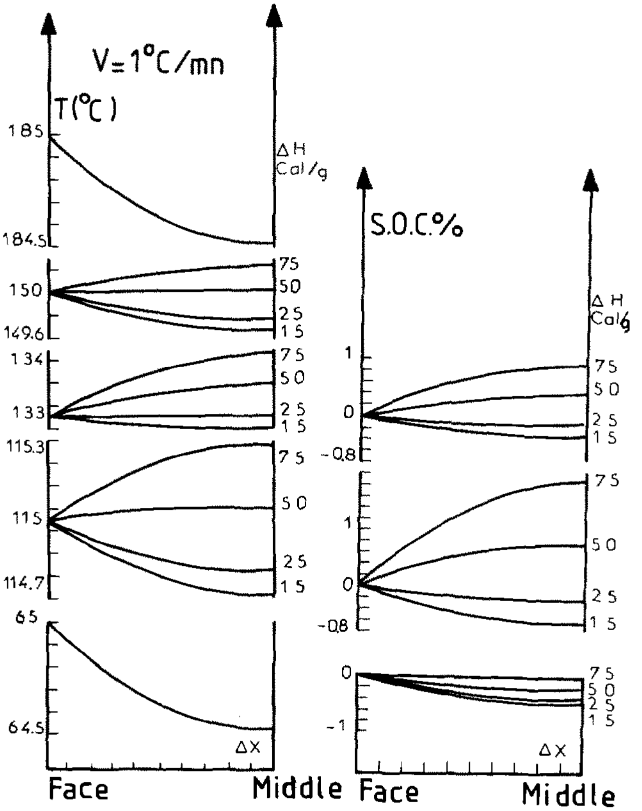

Fig. 11. Profiles of temperature and state of cure developed through the sample at various times and various cure enthalpies: before and after the reaction, at the heat flux maximum and when the heat flux equals half the heat flux maximum. Heating rate = 1° C min^{-1}.

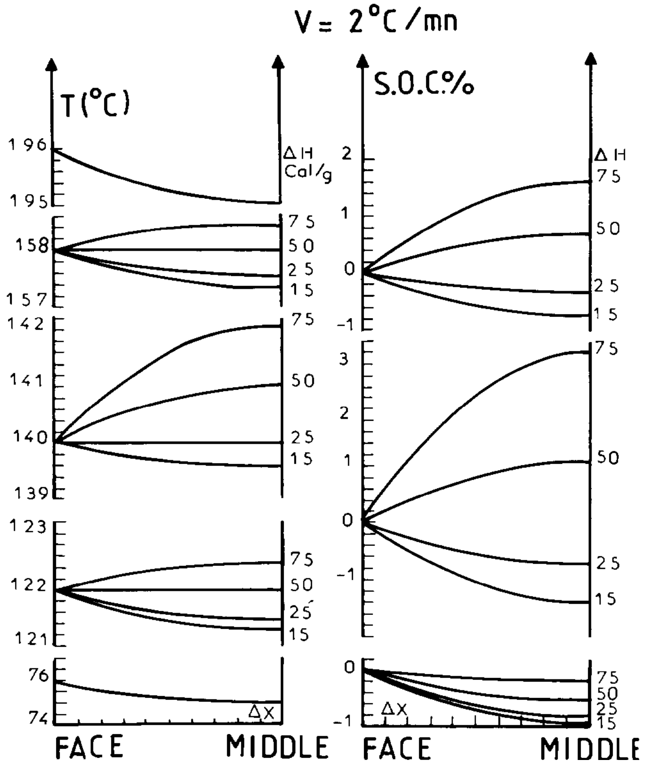

Fig. 12. Profiles of temperature and state of cure developed through the sample at various times and various cure enthalpies: before and after the reaction, at the heat flux maximum and when the heat flux equals half the heat flux maximum. Heating rate = 2° C min^{-1}.

various values of the cure enthalpy (Figs. 7–10). Various conclusions can be drawn from these curves.

(i) There is a good concordance between these curves and the heat flux resulting from the presence of temperature gradients.

(ii) When no reaction occurs, the temperature is higher on the face than at the middle of the sample, because of the time necessary for the heat to be transferred through the sample. This difference in temperature increases proportionally with increasing heating rate of the calorimeter.

(iii) When the reaction takes place, the temperature is increased in the sample because of the exothermicity of the reaction. The highest increase in temperature is obtained at the middle of the sample as shown in Figs. 11–13.

(iv) The increase in temperature at the middle of the sample is proportional to the heat evolved from the reaction, so that it is also proportional to the enthalpy of cure. For a value of 25 cal g^{-1}, the highest value of the temperature at the middle reaches the value of the temperature on the face. Of course, when the cure enthalpy is higher than 25 cal g^{-1}, the value of the temperature at the middle of the sample is higher than that on the face, when the temperature at the middle rises to the maximum.

Profiles of temperature and extent of reaction developed through the sample

The temperature profiles and extent of cure developed through the radius of the sample are drawn at various times, for various values of the enthalpy of cure (Figs. 11–13). These times are chosen in the following way: the first before the reaction takes place, the second when the heat flux is half the highest heat flux value before the maximum value of heat flux, the third at the highest value of the heat flux, the fourth when the heat flux is half the highest value of the heat flux and the last when the reaction is complete. The following results are obtained.

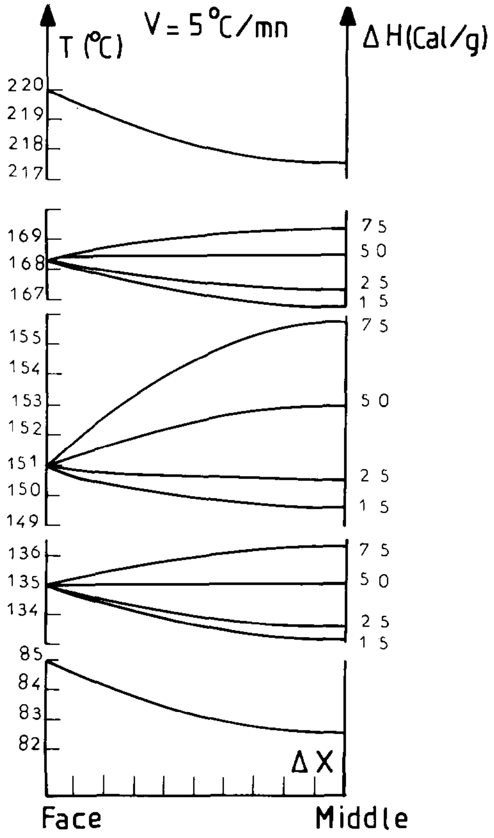

Fig. 13. Profiles of temperature and state of cure developed through the sample at various times and various cure enthalpies: before and after the reaction, at the heat flux maximum and when the heat flux equals half the heat flux maximum. Heating rate = 5 °C $\min^{-1}$.

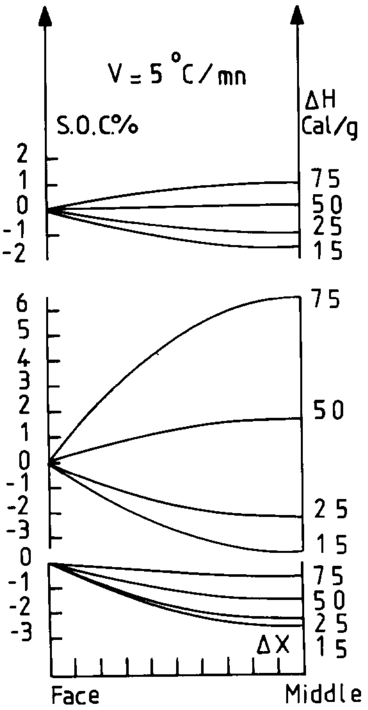

Fig. 13 (continued).

(i) When no reaction occurs, the temperature profiles are the same for various values of the cure enthalpy. The higher the heating rate of the calorimeter, the higher the temperature profile.

(ii) The highest temperature profiles are developed through the sample when the heat flux rises to a maximum. The effects of the cure enthalpy and heating rate on these profiles are illustrated in Figs. 11–13.

(iii) In the same way, the highest profiles of state of cure are developed through the sample when the heat flux rises to its maximum. The higher the enthalpy of cure, the higher the profile of the state of cure.

CONCLUSION

The problem concerned with the advances in the cure process is complicated because of the presence of many factors acting on the calorimeter working in the scanning mode. The present work has afforded a further insight into the effect of the two following parameters: the heating rate of the calorimeter and the enthalpy of cure. These two parameters have been found to be responsible for two different heat transfers.

The first heat transfer is due to the heating of the sample by the calorimeter. Some temperature gradients are developed through the sample, the temperature being higher on the face of the sample. These gradients are proportional to the value given to the heating rate of the calorimeter.

The second heat transfer results from the presence of the internal heat generated by the reaction. This heat is of course transferred from the sample to the calorimeter. The temperature gradients developed through the sample following this heat transfer are proportional to the cure enthalpy and to the value of the heating rate.

As a result, the cure enthalpy acts only on the heat transfer due to the internal heat, while the heating rate plays a role not only on the heat transferred from the calorimeter to the sample but also on the heat due to the reaction.

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