

## **EFFECT OF HEATING RATE IN DSC ON HEAT FLUX–TIME CURVES AND PROFILES OF TEMPERATURE AND STATE OF CURE DEVELOPED IN THE SAMPLE**

G. CHATAING, M. CHATER and J.M. VERGNAUD

*Laboratory of Materials and Chemical Engineering, U.E.R. of Sciences, University of St - Etienne, Saint - Etienne 42100 (France)*

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### **ABSTRACT**

Because of the internal heating arising from the exothermic reaction of thermoset cure and the sample exhibiting a low heat transfer, the applied and measured temperature is the set calorimeter temperature and not the local temperature in the sample during the cure. Moreover, profiles of temperature are developed through the sample studied, with resulting profiles of state of cure. A model has been developed for cylindrical samples in this paper. By taking into account not only the kinetics of heat evolved from the cure reaction but also the parameters of heat conduction through the sample and the cell–sample interface, heat flux–time curves as well as the profiles of temperature and state of cure developed through the sample can be predicted by calculation. The effect of the heating rate chosen for DSC experiments on these profiles of temperature and state of cure has been especially studied.

### **INTRODUCTION**

In the DSC technique, the rate of enthalpy change accompanying the chemical event in the sample is monitored as a function of temperature, while the sample is heated at a known linear rate.

Several sources of error can arise from different factors.

(i) Because of the heat evolved from exothermal reactions and low heat conductivity of the material, very high gradients of temperature are developed through the sample [1,2], especially for reactions of high enthalpy. Moreover, the applied temperature is the set calorimeter temperature and not the resin temperature during cure.

(ii) A good contact must be made between the resin and the sample holder [3], and we have noticed the importance of the quality of contact between the holder and the calorimeter vessel [4,5].

(iii) Dispersion problems occasionally arise and are generally observed by lack of reproducibility. The question is: how representative is a very small sample (2–5 mg), taken from a large batch, of the homogeneity of the batch?

A larger size (100–200 mg) could perhaps be useful in reducing this effect due to lack of homogeneity. Unfortunately, however, the larger the sample size, the higher the gradients of temperature developed through the resin during cure. The value of the heating rate is also of great importance.

Our purpose in this work is to study the events occurring throughout the resin sample during cure with a rather larger sample (100–200 mg) and to determine the effect of the value chosen for the heating rate. The heat flux transferred through the sample–calorimeter interface has been calculated during the cure, as well as the profiles of temperature and state of cure obtained throughout the resin.

A model previously described for sheets [1–6] has been applied to a cylindrical sample, in which radial heat is conducted through the circular cross-section. It also takes into account the heat evolved by the cure reaction whose kinetics were determined.

## THEORETICAL

### *Mathematical treatment*

The equation of heat conduction through the cross-section reduces to

$$\rho C \frac{\partial T}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left( r \lambda \frac{\partial T}{\partial r} \right) + \rho \frac{dQ}{dt} \quad (1)$$

where the contribution for the increase in temperature due to heat conduction and heat from the cure reaction can be seen.

The rate of the overall cure reaction is given by a simple equation

$$\frac{dQ_{r,t}}{dt} = K_0 (Q_\infty - Q_{r,t}) \exp(-E/RT) \quad (2)$$

### *Numerical analysis*

The problem cannot be solved by a mathematical treatment, and the solution is given by a numerical method with finite differences.

If we consider different circles of radius  $r - \Delta r$ ,  $r + \Delta r$ , etc., taken on a circular cross-section ( $r$  being between 0 and  $R_s$ , the radius of the sample), the heat balance determined for the ring between  $r - \Delta r/2$  and  $r + \Delta r/2$  gives

$$T_{i+1,r} = \frac{1}{M} [T_{i,r+\Delta r} + (M-2)T_{i,r} + T_{i,r-\Delta r}] + \frac{\Delta r}{2M_r} [T_{i,r+\Delta r} - T_{i,r-\Delta r}] + \frac{1}{C} \frac{dQ}{dt} \Delta t \quad (3)$$

where  $T_{i+1,r}$  is the temperature at radius  $r$  after the elapse of time  $(i+1)\Delta t$ .

The increments of time and space are combined in eqn. (4),  $M$  being a dimensionless number.

$$M = \frac{(\Delta r)^2}{\Delta t} \frac{1}{\alpha_s} \quad (4)$$

For the middle of the cylinder,  $r=0$ , another equation has been found suitable for calculating temperatures.

$$T_{i+1,0} = \frac{4}{M}(T_{i,\Delta r} - T_{i,0}) + \frac{1}{C} \frac{dQ}{dt} \Delta t \quad (5)$$

A convenient equation has been used for the calorimeter-sample interface [7].

$$T_{i+1,R} = \frac{H}{1+H} T_{i,m} + \frac{1}{1+H} T_{i,R} \quad (6)$$

by evaluating the coefficient  $H$

$$H = \left( \frac{\alpha_m}{\alpha_s} \right)^{1/2} \frac{\lambda_s}{\lambda_m} \quad (7)$$

The heat flux (HF) transferred through the sample-calorimeter interface is obtained as follows

$$\text{HF} = \lambda_s \frac{T_R - T_{R-r}}{r} \quad (8)$$

The cure reaction is calculated by a recurrent relation [1,2].

## EXPERIMENTAL

The apparatus (DSC 111, Setaram) is used in scanning mode with various values for the heating rate ranging from 5 to 20°C min<sup>-1</sup>.

The sample (150–200 mg) in aluminium holder of radius 0.25 cm is scanned for a first cure, then cooled to room temperature, and rescanned under the same conditions giving the baseline.

Parameters for cure reaction and heat transfer are shown in Table 1.

TABLE 1

### Material properties

Kinetic parameters:  $n=1$ ;  $K_0=300000 \text{ s}^{-1}$ ;  $E=15 \text{ kcal mol}^{-1}$

Cure enthalpy:  $Q_\infty=65 \text{ cal g}^{-1}$

Heat transfer:  $\lambda=10^{-3} \text{ cal s}^{-1} \text{ cm}^{-1} \text{ K}^{-1}$ ;  $C=0.32 \text{ cal g}^{-1} \text{ K}^{-1}$

$\alpha=25 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$

Increments for calculation:  $\Delta r=0.025 \text{ cm}$ ;  $\Delta t=0.05 \text{ s}$ ;  $H=1$ ;  $M=5$

## RESULTS AND DISCUSSION

In this paper, devoted to the DSC technique and the effect of heating rate, we will successively determine: heat flux–time curves, profiles of temperature and state of cure developed in various parts of the resin sample as a function of time.

*Heat flux–time curves*

Heat flux–time curves obtained with the model and especially with eqn. (8), are in good agreement with the experimental curves, except perhaps a slight change in the slope of the baseline corresponding to the variation in thermal properties of the material with temperature. Figure 1 illustrates typical heat flux–time curves obtained with various heating rates. The effect of heating rate on some parameters of interest is clearly shown in this figure.

(i) Increase in sensitivity (measured by heat flux value) with heating rate, with a constant factor of proportionality.

(ii) Decrease in the width of heat flux–time curves with heating rate, the area under heat flux–time curves (or cure enthalpy) remaining constant.

*Profiles of temperature and state of cure*

The profiles of temperature obtained in various positions within the cross-section of the samples can be appreciated in Fig. 2 as a function of time, for the values chosen for the heating rate. These profiles of temperature vary with time, and the effect of heating rate is of importance: the higher the heating rate, the higher the gradients of temperature throughout the sample, with an approximately constant coefficient of proportionality.

The maximum for heat flux is obtained at about the same time as the maximum of the temperature determined in the sample, and Figs. 1 and 2

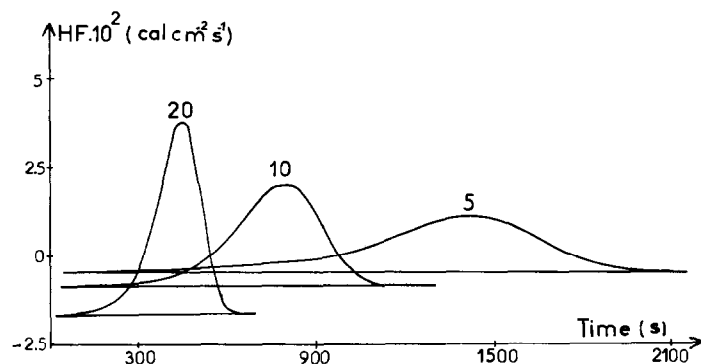


Fig. 1. Heat flux–time curves for various heating rates: 20, 10 and 5°C min<sup>-1</sup>.

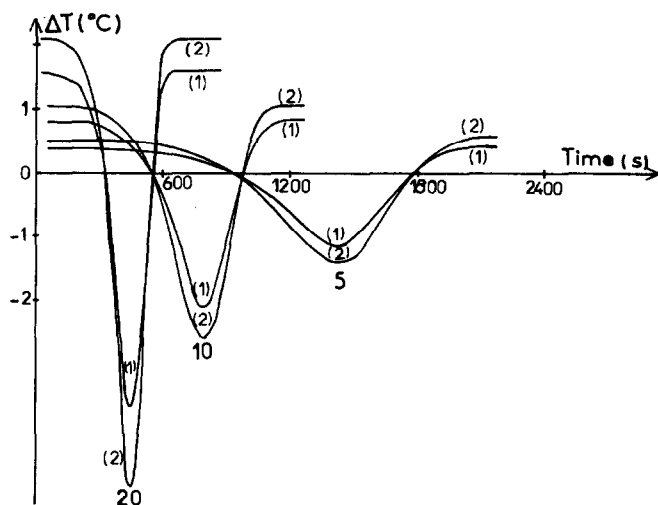


Fig. 2. Profiles of differences of temperature through the sample for various heating rates: 20, 10 and  $5^{\circ}\text{C min}^{-1}$ . (1)  $T_{\text{face}} - T_{R_s/2}$ ; (2)  $T_{\text{face}} - T_{\text{middle}}$ .

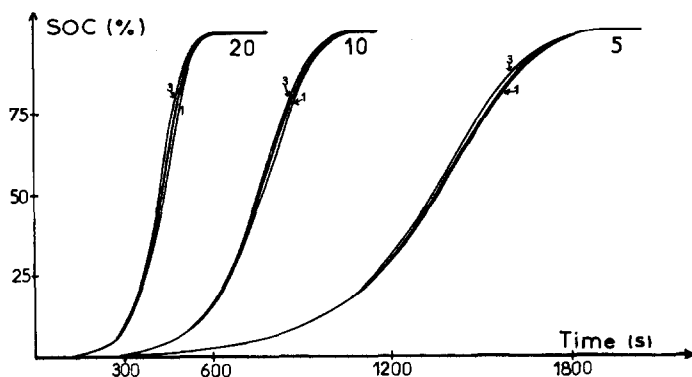


Fig. 3. Profiles of SOC through the sample for various heating rates: 20, 10 and  $5^{\circ}\text{C min}^{-1}$ . (1) Face; (2) (centre curve)  $r = R_s/2$ ; (3) middle.

illustrate this point. Of course, the higher the gradient of temperature, the higher the heat flux measured by the calorimeter.

The profiles of state of cure with time are illustrated in Fig. 3 at various places through the sample cross-section, for different values of heating rate. Of course, some gradients of state of cure can be shown for high values of heating rate.

## CONCLUSIONS

A high value for the heating rate in the DSC technique is of interest for increasing the sensitivity of heat flux-time curves. However, when the

enthalpy of reaction is high (higher than 20 cal g<sup>-1</sup> for instance), as this paper was careful to point out, several drawbacks appear with high gradients of temperature developed throughout the sample followed by gradients of state of cure. There is no doubt that an increase in the size of the sample, perhaps allowing more accurate measurements if the homogeneity of the material is concerned, is also responsible for higher gradients of temperature. A compromise must be chosen for determining the value of heating rate and the following law may perhaps be of interest

$$(\text{sample dimension})^2 \times (\text{heating rate}) = \text{constant}$$

In fact, this problem is not so simple and the whole phenomenon must be considered in further enhanced studies. Several parameters play an important role, and not only the dimensions of the sample and heating rate, but also the enthalpy, and perhaps the kinetics of reaction, must be considered. This model could particularly be applied to larger samples, where it would be very useful in industrial applications, if the samples could be considered as semi-plant scale.

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