

EFFECT OF HEATING RATE ON THE SEPARATION OF VARIOUS PHENOMENA IN THE DSC TECHNIQUE

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ABSTRACT

The value chosen for the heating rate plays an important role in the DSC technique. For example, the use of a low heating rate is of great help in determining the kinetic parameters of reactions more clearly. In this paper, the separation of peaks corresponding to heat flux–time curves of two various phenomena is especially studied. These peaks are shown in a typical cure reaction of epoxy resins. After determination of the kinetic parameters, DSC curves are simulated and a good agreement is found between theoretical and experimental curves. The effect of the heating rate on the separation factor of these peaks is studied, as well as its effect on the sensitivity of heat-flux measurement.

INTRODUCTION

Several studies of the reaction kinetics of epoxy cure by means of differential scanning calorimetry have been performed [1,2], and an excellent review of the kinetics of thermoset cure has been recently written [3,4]. By assuming that the rate of enthalpy change is proportional to the rate of cure reaction, kinetic parameters have been determined from the enthalpy changes monitored by DSC. Although the reaction is perhaps complex, it has very often been described by means of a simple n th-order kinetic expression governed by a single activation energy [2,5]. Because of local heating, arising from exothermic reactions and low heat transfer through the material [6], some profiles of temperature can be developed through the sample, and the measured temperature is the set calorimeter temperature and not the true temperature during cure. Nevertheless, the temperature considered in kinetic studies is the set calorimeter temperature.

Different methods of kinetic evaluation are usually used for determining kinetic parameters from DSC experiments [7,8]. However, these parameters are proved to be valid when simulated and experimental DSC curves coincide well.

The purpose of this work is to determine all the kinetic parameters of

reactions when several peaks can be distinguished in DSC curves. Very often, these peaks are very close, and it is only possible to appreciate a disturbance in the shape of the peak representing heat flux–time curves. In this paper a parameter concerned with the DSC technique is especially studied: the heating rate chosen for the calorimeter and sample. The effect of this parameter on the shape of heat flux–time curves is evaluated, by considering the quality of separation of two heat flux–time peaks occurring for particular epoxy resins, and the value of the heat flux which is the best measure of DSC sensitivity.

EXPERIMENTAL

Materials

The formulations used in this study were composed of 2608 epoxy resin (CDF Chimie) which basically contains DGEBA epoxy molecules, an anhydride hardener, with tertiary amine as catalyst. The formulation investigated contained 80 parts of hardener per hundred parts of resin, by weight.

The epoxy amine mixtures were prepared by heating the resin to room temperature and adding the curing agent with continuous stirring until a clear mixture was obtained. Reactions during mixing were negligible as confirmed by DSC measurements. The mixture was then stored in the refrigerator and tested.

Techniques

The mixture was removed from the refrigerator and allowed to warm to room temperature. Samples of about 150 mg were placed in hermetically sealed iron-steel holders, Calorimetric measurements were made with a DSC III (Setaram, France), by using various values for the heating rate, ranging from 0.5 to 20°C min⁻¹. The temperature was programmed from 30 to about 250°C. After cooling the calorimeter and sample to room temperature, the calorimeter is heated again under the same conditions in order to obtain the baseline for heat flux–time curves.

The cylindrical sample, with an external diameter of 5.1 mm, is placed in the vessel close to the heat-flux detector.

Calculations

Heat flux–time curves were obtained by calculation using a Hewlett-Packard 86, after storing data and determining the kinetic parameters with the help of the Freeman–Carroll method. The validity of these kinetic data

was controlled by superimposing heat flux–time curves obtained by calculation and experimentally.

RESULTS

Determination of the kinetic parameters

The reaction rate equation used in this study was

$$\frac{dy}{dt} = K_0(1 - y)^n \exp - \frac{E}{RT} \quad (1)$$

where y is the extent of reaction, K_0 the frequency factor, E the activation energy and n the order of the overall reaction.

With the above assumption, the extent of reaction is given as follows

$$y = \frac{Q_t}{Q_\infty} \quad (2)$$

where Q_t is the heat evolved from the cure reaction up to time t , and Q_∞ is the total cure enthalpy.

Experimental heat flux–time curves are then described by eqn. (1) under these conditions.

Experimental heat flux–time curves obtained with a heating rate of 2°C min^{-1} were studied using the Freeman–Carroll method. This method generally gives an accurate value for the activation energy (slope of the curve), but a poor value for the order (coordinate intercept). The frequency factor is determined by adjusting the heat flux calculated with the above values for the order and activation energy and the corresponding heat flux obtained by experimentation at different temperature.

The rather poor agreement has been found between experimental heat flux–time curves and calculated curves by using these values for kinetic parameters (Table 1, first line). Although the maximum of the heat flux–time curve is well positioned, the shape of the tail at the end of the peaks (for

TABLE 1
Kinetic parameters

K_0	E	n
<i>Large peak</i>		
3.58×10^{12}	27.966	1.25
3.58×10^{12}	27.966	$1.25 - n = 1.1$
3.58×10^{12}	27.966	1.1
<i>Small peak</i>		
4.75×10^{76}	155.000	2.75

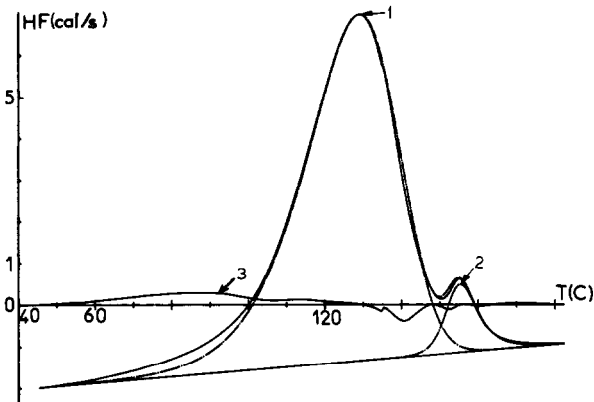


Fig. 1. Heat flux-time curves: experimental (—) and theoretical (---). $2^{\circ}\text{C min}^{-1}$, abscissa: temperature. Peak 1 = peak 2 minus peak 3 = difference between experimental and theoretical results. $\text{HF} \times 100$.

50°C higher than 80%) is not exactly the same, when these peaks are calculated or obtained experimentally.

A better agreement has been obtained by varying the value for the order from 1.25 to 1.1 continuously, while the other kinetic parameters are kept constant. The order has been changed from the time at which the state of cure is 45% to the time corresponding to a state of cure of 75%.

However, the best agreement between simulation and experiment can be appreciated when the value of the order is lowered (Table 1, line 3). The reason for this fact is very clear if eqn. (1) describing the heat flux-time curves is considered. The effect of the value taken for the order on the shape of these curves is negligible when the state of cure is low (for instance lower than 40%), but becomes of higher importance as the state of cure increases.

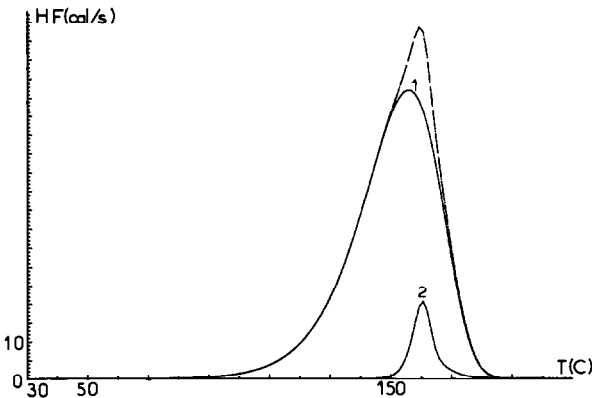


Fig. 2. Heat flux-time (temperature) curves. $20^{\circ}\text{C min}^{-1}$. Peak 1 plus peak 2 = total heat flux-temperature curve. $\text{HF} \times 100$.

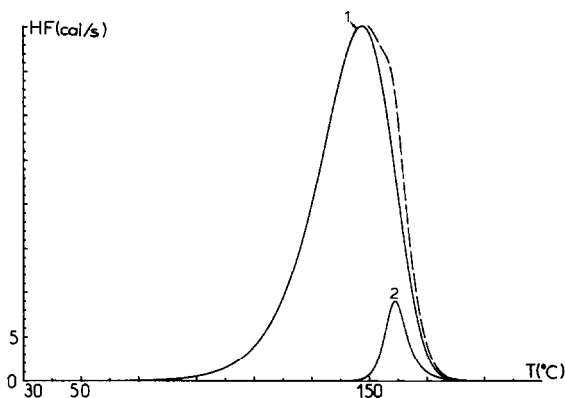


Fig. 3. Heat flux–time (temperature) curves. $10^{\circ}\text{C min}^{-1}$. Peak 1 plus peak 2 = total heat flux–temperature curve. $\text{HF} \times 100$.

For the smaller peak shown at higher temperature, corresponding to an unknown exothermic event, the kinetic parameters of a reaction having the same effect have been found as in Table 1, line 4. Because of the particularly low value for the width of the heat flux–time curves, a very high value has to be found for the activation energy, followed by a high value for the frequency factor.

Effect of heating rate on peak separation

Two phenomena are represented by two peaks in Fig. 1, when the heating rate is $2^{\circ}\text{C min}^{-1}$.

By using the kinetic parameters shown in Table 1, heat flux–time curves have been calculated for various heating rates ranging from 0.5 to $20^{\circ}\text{C min}^{-1}$.

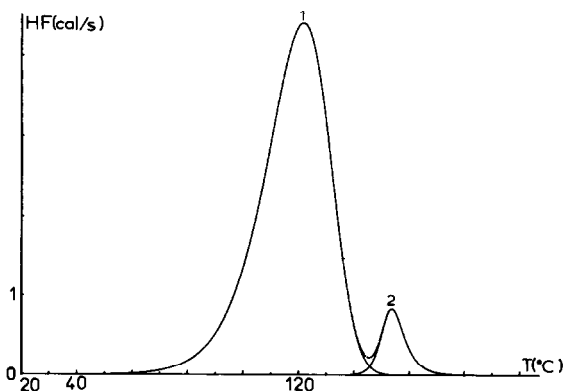


Fig. 4. Heat flux–time (temperature) curves. $1^{\circ}\text{C min}^{-1}$. Peak 1 plus peak 2 = total heat flux–temperature curve. $\text{HF} \times 100$.

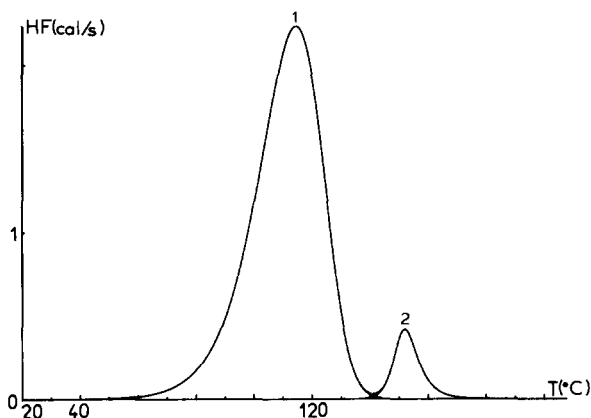


Fig. 5. Heat flux–time (temperature) curves. $0.5^{\circ}\text{C min}^{-1}$. Peak 1 plus peak 2 = total heat flux–temperature curve. $\text{HF} \times 100$.

Of course, the lower the heating rate, the better the separation obtained for these peaks. For the higher heating rate ($20^{\circ}\text{C min}^{-1}$), the small peak is located under the large one, and the total peak resulting from the addition, which can be observed experimentally, exhibits a particular shape, but no separation is observed (Fig. 2). The shape of the total peak is slightly affected when the heating rate is $10^{\circ}\text{C min}^{-1}$ (Fig. 3). A visible separation can be appreciated at a heating rate of $2^{\circ}\text{C min}^{-1}$ (Fig. 1), and a complete separation is obtained with lower heating rates (Fig. 4, $1^{\circ}\text{C min}^{-1}$; Fig. 5, $0.5^{\circ}\text{C min}^{-1}$).

The separation factor F is determined as follows for these peaks

$$F = \frac{T_{m1} - T_{m2}}{\Delta T_1 + \Delta T_2} \quad (3)$$

where T_m is the temperature obtained for the maximum heat flux, and ΔT is the width of the peak expressed in degrees (in fact, the width at half height is measured as $\Delta T/2$).

A value higher than 1 for the separation factor corresponds to a complete separation, but a value of about 0.7 allows the operator to distinguish the presence of two distinct phenomena.

The variation of the separation factor with heating rate is of interest (Fig. 6) when distinct phenomena must be distinguished and studied. Of course, the lower the heating rate, the higher the value of the separation factor.

Although a decrease in the value for the heating rate of DSC improves the separation factor, it is also responsible for various drawbacks:

(1) a simultaneous decrease in the sensitivity measured by the value of heat flux, as shown in Fig. 6, while the total cure enthalpy remains about constant;

(2) a following large increase in the time needed for experiments.

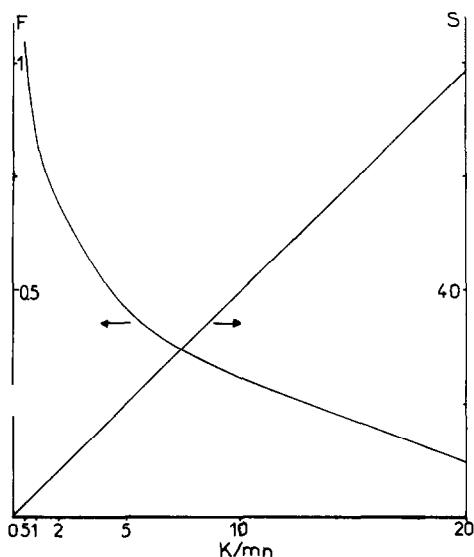


Fig. 6. Variation of the separation factor and maximal heat flux with heating rate of DSC.

Moreover, high heating rates are also responsible for the development of high gradients of temperature throughout the sample, provoking another disturbance in heat flux–time curves. These gradients of temperature have been found of importance for high heating rates and large samples, particularly when the cure enthalpy is higher than 20 cal g^{-1} [9,10].

CONCLUSIONS

The effect of the value of the heating rate in DSC on various factors has been qualitatively studied in this paper: the separation of two different phenomena, the sensitivity of the technique by considering the value of heat flux.

The separation factor has been introduced for qualifying the degree of separation of two peaks expressing heat flux–time profiles for two various phenomena. These phenomena have been considered as simple reactions with a constant activation energy.

The increase in the separation factor following the decrease in the heating rate has been determined for typical heat flux–time curves obtained with a particular epoxy resin.

The decrease in the value of the heating rate in DSC is responsible for various effects:

- (1) an increase in the separation factor when two different phenomena occur in the sample;
- (2) a decrease in the sensitivity of the technique measured by the value of

the heat flux;

(3) an increase in the time for experiments.

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