VALUES OF KINETIC PARAMETERS OF CURE REACTION OF EPOXY IN CALORIMETRY BY DC AND DSC

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ABSTRACT

A fundamental study to determine the best kinetic parameters of reaction in calorimetry has been carried out. The amount of material used in the sample, as well as the mode of calorimetry, have been considered. The process in calorimetry is complex because the convective heat transfer is superimposed on the heat transfer due to the reaction. With constant temperature operations in the DC mode, the process occurs with a strong heating period up to the establishment of equilibrium, followed by a reactive period with an increase in temperature. In the DSC mode, the temperature in the sample is lower than in the calorimeter, and the reaction causes an increase in temperature. Despite these inconveniences, DSC is the better mode for determining kinetic parameters. As a result, the kinetic parameters of the cure reaction of epoxy resin determined by DC and DSC techniques are not the same.

LIST OF SYMBOLS

C, C_1, C_2	specific heat of sample, holder and air respectively
E	activation energy
K_0	rate constant of reaction
M, M_1, M_2	moduli for calculation $M_1 = \dfrac{\rho_1 C_1 \left(\Delta r_1\right)^2}{\lambda_1 \, \Delta t}$
n	order of overall reaction
Q_∞	enthalpy of reaction
Q_t	enthalpy evolved up to time t
R	radius of sample
R_1, R_2	radial thickness of holder and air respectively
Δr, Δr_1, Δr_2	finite increment in radius of sample, holder and air respectively
SOC	state of cure reaction
Δt	finite increment in time
T_M	temperature of mould

T_j, TN_j	temperature of jth increment at time t and $t + \Delta t$ respectively
V	rate of heat evolved per unit of mass
λ, λ_1, λ_2	thermal conductivity of sample, holder and air respectively
ρ, ρ_1, ρ_2	density of sample, holder and air respectively

INTRODUCTION

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

Of course, both techniques exhibit some advantages and disadvantages, and the user has to select the better technique according to his own purpose. In general, DC is considered to be easy to work with. The advantages of the constant temperature operation in the DC mode are:

(1) It is easy to use because the calorimeter is stabilized at the desired temperature and the sample at room temperature is introduced as the time-base recording is started.

(2) The DC mode appears more straightforward than the DSC one, possibly because of working at a constant temperature.

In fact, these advantages are not in accordance with reality and there are many drawbacks to the DC mode:

(1) In a DC experiment, the enthalpy of reaction occurring at the applied temperature up to a given time is determined. But the applied temperature is not the true sample temperature, either during the heating period, because of the time required for the sample to establish thermal equilibrium after introduction, or during reaction, because of local heating arising from the exothermic reaction.

(2) Three experiments at various temperatures are required in order to determine the kinetic parameters, especially the activation energy and rate constant. A temperature window width is always found over which meaningful data can be obtained, this window width being about 20°C for rubber [1,2] or thermosetting materials [3]. The highest temperature at which measurements can be obtained is determined by the induction period required for the cure reaction to initiate [1]. If the induction period is shorter than the time required for establishment of thermal equilibrium after introduction of the sample, this first part of the cure exotherm is not obtained. The lowest temperature is determined by the calorimeter sensitivity.

(3) In the DC mode the sample undergoes a complicated process, and two (or three) steps can be distinguished [4,5]: the heating period when the sample is introduced, characterized by very high temperature gradients in

the sample [4,5] and then the reaction period with an increase in temperature over that of calorimeter due to local heating arising from the reaction; a maximum in the enthalpy change (the reaction rate) is observed during this second step.

(4) Because of the above facts, the temperature of the sample equals that of the calorimeter at two points: when the enthalpy rate reaches zero at the end of the first period and at the end of the second period when the reaction is over [6].

The main purpose of this paper has been to determine the kinetic parameters of reaction when working in the DC mode, and to compare them with the actual reaction parameters obtained by DSC.

The second purpose of this work has been to demonstrate that such a difficult problem can be resolved by using a mathematical model. These models, based on numerical methods with finite differences, consider all of the variables, not only the kinetics of the reaction but also the heat transferred by conduction through the sample, metal holder [4,5] and even the air layer located between the holder and calorimeter [6]. The kinetics of the reaction were previously determined using DSC experiments with a selected heating rate [7,8]. The reaction chosen for this study is the curing of epoxy resin.

EXPERIMENTAL

Apparatus

A DSC 111 calorimeter (Setaram, Lyon, France) was used either in scanning mode or under isothermal conditions. The sample size was rather large (150 mg) and the dimensions of the metal holder were 0.5 cm internal diameter and 0.7 cm external diameter. The thickness of the air layer between the holder and calorimeter was 0.027 cm.

The kinetic parameters of the reaction were determined by the apparatus in scanning mode with a heating rate of $2°C$ min^{-1}. This heating rate has been found convenient for this high enthalpy reaction [7–9].

TABLE 1

Thermal properties of materials

	ρ (g cm^{-3})	λ (cal cm^{-1} s^{-1} °C^{-1})	C_p (cal g^{-1} °C^{-1})
Resin	1.47	8×10^{-4}	$0.3 + (5 \times 10^{-4})T$ [a]
Air (125°C)	0.944×10^{-3}	7.6×10^{-5}	0.24
Metal	7.86	0.107	0.108

[a] T in °C.

Material and properties

The cure reaction of eposy resin has a high enthalpy. The kinetic parameters of the reaction are $n = 1.56$, $K_0 = 2 \times 10^{23}$ s^{-1}, $E = 50\,018$ cal mol^{-1} and $Q_\infty = 38$ cal g^{-1}. The thermal properties of all the materials, air, holder and resin, are shown in Table 1.

THEORETICAL

Assumptions

Some assumptions were made in order to apply the mathematical model to the problem:
(1) Only radial heat through the circular cross-section was considered because of the cylindrical shape of the sample and holder, and of the disposition of the sensitive heat cell of the calorimeter.
(2) The thin layer of air between the sample and calorimeter is cylindrical in shape with a constant thickness, the holder being well centred in the calorimeter.
(3) The holder also has a constant thickness.
(4) The temperature of the calorimeter (heated oven and sensitive cell) was constant, even when the sample previously at room temperature was introduced, and when internal heat was evolved due to the reaction.
(5) The heat evolved from the cure reaction is expressed by a simple equation with an Arrhenius form, and with constant kinetic parameters.

Mathematical treatment of the process (heating and cure)

The increase in temperature at any place in the sample is given by the general equation for transient heat conduction

$$\rho C \frac{\partial T}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left[r\lambda \frac{\partial T}{\partial r} \right] + \rho \frac{dQ}{dt} \tag{1}$$

where the contribution of the heat transferred by conduction and of the heat evolved from the cure reaction can be seen in the right hand of this equation. Initial and boundary conditions are

$$t = 0 \begin{cases} 0 \leqslant r \leqslant R & T \text{ sample} \\ R \leqslant r \leqslant R_1 + R & T \text{ holder} \\ R + R_1 < r < R_2 + R_1 + R & T \text{ air layer} \end{cases} \tag{2}$$

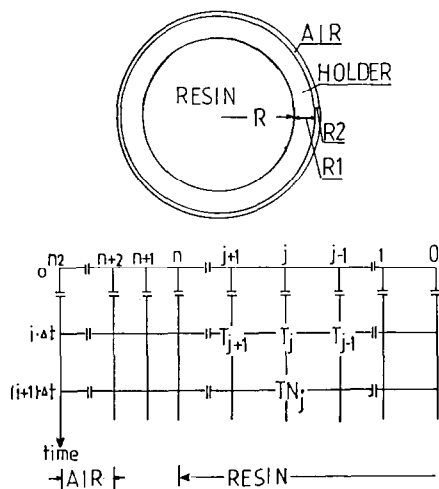$$t > 0 \quad r = R_2 + R_1 + R \qquad T \text{ mould} \tag{3}$$

Fig. 1. Scheme for numerical analysis.

The equation for the rate of heat evolved from the cure reactions is

$$\frac{1}{Q_\infty} \frac{dQ_t}{dt} = K_0 \left(1 - \frac{Q_t}{Q_\infty}\right)^n \exp\left(-\frac{E}{RT}\right) \tag{4}$$

Numerical analysis

No analytical solution can be found to the problem, and a numerical method with finite differences has been used. The circular cross-section of the sample, holder and air layer is shown in Fig. 1, as well as the circles of radii $r - \Delta r$, r, and $r + \Delta r$. The heat balance in the ring located between the circles $r - \Delta r/2$ and $r + \Delta r/2$ has been calculated by considering the heat from conduction and cure reaction in the sample and the heat conduction in the holder and air. As a result, the temperature in the ring after an elapse of time Δt has been obtained as a function of the temperature at the preceding time in the ring and in the two adjacent rings.

Within the resin, with $1 \leqslant j \leqslant N - 1$

$$TN_j = \frac{1}{M}\left[T_{j-1} + (M-2)T_j + T_{j+1}\right] + \frac{1}{2jM}(T_{j+1} - T_{j-1}) + \frac{1}{C}\frac{dQ}{dt}\Delta t \tag{5}$$

and in the middle of the resin, $j = 0$

$$TN_0 = T_0 + \frac{4}{M}(T_1 - T_0) + \frac{1}{C}\frac{dQ}{dt}\Delta t \tag{6}$$

within the metal holder, with $N + 1 \leqslant j \leqslant N_1 - 1$

$$TN_j = \frac{1}{M_1}\left[T_{j-1} + (M_1 - 2)T_j + T_{N+1}\right] + \frac{\Delta r_1 (T_{j+1} - T_{j-1})}{2M_1(R + (j - N)\Delta r_1)} \tag{7}$$

Within the layer of air, with $N_1 + 1 \leqslant j \leqslant N_2 - 1$

$$TN_j = \frac{1}{M_2}\left[T_{j-1} + (M_2 - 2)T_j + T_{j+1}\right] + \frac{\Delta r_2(T_{j+1} - T_{j-1})}{2M_2\left[R + R_1 + (j - N_1)\Delta r_2\right]} \qquad (8)$$

Other more complicated relations have been obtained for the temperature at the interfaces, between the sample and metal for $j = N$ and between the air and metal holder with $j = N_1$, as well as the interface between the mould and air layer, as shown previously [6].

The conditions for stability of the calculation are

$$M > 4, \ M_1 > 2 \text{ and } M_2 > 2 \qquad (9)$$

and two other conditions as shown previously [5].

Heat evolved from the cure reaction

The heat generated by the cure reaction at time t is obtained with the recurrent relation, with $t = i\,\Delta t$

$$Q_{i+1} = Q_i + \left(\frac{dQ}{dt}\right)_i \Delta t \qquad (10)$$

with

$$\left(\frac{dQ}{dt}\right)_i = K_0\left(1 - \frac{Q_i}{Q_\infty}\right)^n Q_\infty \exp\left(-\frac{E}{RT_i}\right) \quad \text{and} \quad Q_0 = 0 \qquad (11)$$

The state of cure (SOC) is as follows

$$SOC_i = \left[\frac{Q_i}{Q_\infty}\right]100 \qquad (12)$$

Heat flux emitted through the mould surface

The heat flux is determined near the surface of the resin

$$HF = \lambda\left(\frac{3T_R - 4T_{R-\Delta r} + T_{R-2\Delta r}}{2\Delta r}\right) \qquad (13)$$

and

$$V = HF\frac{2\pi R}{\pi R^2 \rho} \qquad (14)$$

RESULTS

Statement of the problem

As shown previously, the temperature of the calorimeter is not the actual temperature applied to the sample. Moreover, the temperature is not the

same throughout the sample, either in DC or DSC. In fact high temperature gradients develop in a complex manner for both DC and DSC.

DC mode

In the case of DC, steep temperature gradients are developed very quickly during the first heating step when the sample is introduced into the calorimeter, because of the rather low rate of heat transfer due to the low heat conductivity of the material (especially organic material such as elastomers, polymers and thermosets). These high temperature gradients are increased with the higher temperature on the surface of the sample near the calorimeter. There are two consequences of this:

(1) Very high heat flux values are obtained during this heating period which represents the time necessary for the sample to reach thermal equilibrium. Because of this high endothermic heat flux, the beginning of the reaction may be unobserved, especially at high temperatures. This is important in the case of initiated reactions (elastomers, thermosets).

(2) Because of the internal heat generated by the reaction, an increase in temperature occurs in the sample so that other temperature gradients are set up within the sample during the reaction. Thus, the sample temperature is not the same as that of calorimeter, nor is it constant during the reaction or the same throughout the sample.

DSC mode

In the DSC mode, because of the rate of heating of the calorimeter and the rate of heat transfer by conduction through the sample, the temperature in the sample is lower than that of calorimeter, this shift being proportional to the heating rate and the square of the main dimension of the sample [10].

Moreover, there is an increase in the sample temperature caused by the exothermicity of the reaction. Thus, in DSC the sample temperature is not equal to the temperature of the calorimeter although this temperature shift towards lower values than those recorded can be reduced by using a lower heating rate, if the sensitivity of the measurement permits.

Either simple models based on the equality of temperatures of the sample and calorimeter [11–14], or more complex models which take into account the heat transfer by conduction as well as the internal heat generated by the reaction [7–9] can be used. In fact, the rate of heat transfer by conduction must be introduced in the model when the heating rate of calorimeter is high, and this conductive heat transfer can be eliminated when the heating rate is low. The right value of the heating rate is not subjective, but can be selected with the knowledge of various relationships [7–9] which account for the sample size and consider the value of the enthalpy of reaction.

In consequence, the parameters characterizing the kinetics of the reaction may differ depending on the method of their determination.
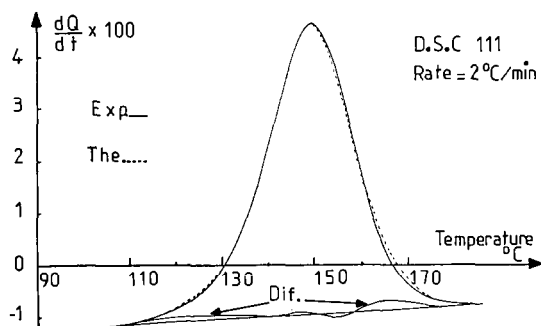
Fig. 2. Heat flux–temperature profiles in DSC: ———, experimental; – – –, calculated.

Modelling the process of heating and the reaction

It is a difficult and complex problem to determine how the kinetic parameters have been altered by the whole process taking place in DC mode. The single key to this problem has been to use modelling of the process.

By using the mathematical model which takes into account not only the kinetics of the reaction (heat evolved) but also the rate of heat transfer by conduction, the heat flux–time histories have been calculated in DC. The comparison of the calculated and experimental heat flux–time histories was used to test the validity of the model as well as the quality of the kinetic parameters.

The kinetic parameters of the reaction were determined from DSC experiments run with a low heating rate using the simple model. The quality of the parameters obtained has been tested by considering the overlap of the calculated and experimental heat flux–temperature histories (Fig. 2).

The heat flux–time history obtained by calculation with the model described in the paper and with the parameters obtained from DSC experiments (Table 1) has been drawn in Fig. 3. This curve is in good agreement with that obtained experimentally under the same temperature conditions (150 °C) [6].

Heat flux–time and temperature–time histories

As shown in the theoretical section above, the model can give the heat flux emitted at the surface of the sample and also the temperature profiles developed through the sample.

The heat flux–time histories have been drawn for various temperatures of the calorimeter (140 °C in Fig. 4, 160 °C in Fig. 3 and 150 °C in Fig. 5) as well as the temperature obtained at the centre of the sample. Although these profiles are not exactly the same, they are similar in shape and they pass through a maximum at about the same time. The following observations can
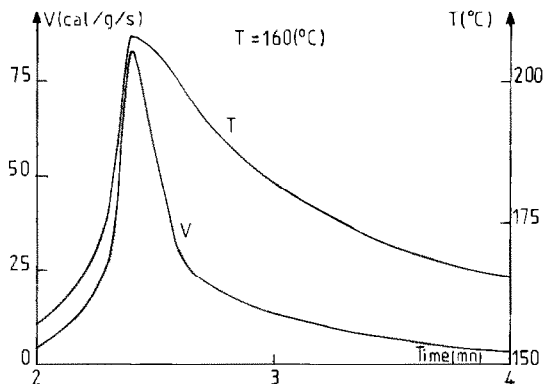
Fig. 3. Heat flux–time profile in DC at 160°C (scale on the left) and temperature in the centre of the sample–time history (scale on the right).
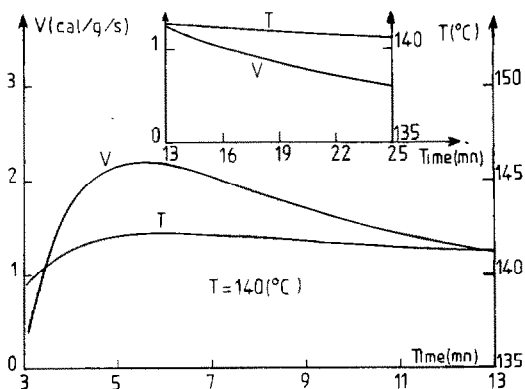

Fig. 4. Heat flux–time profile in DC at 140°C (scale on the left) and temperature in the centre of the sample–time history (scale on the right).
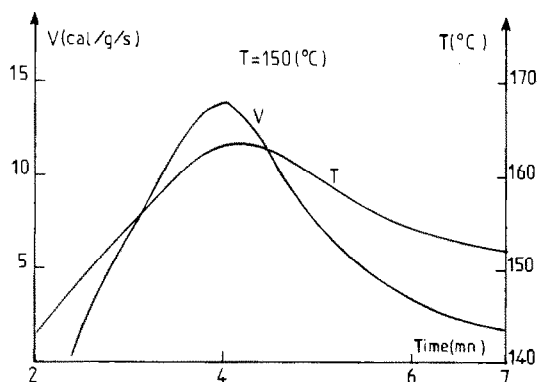

Fig. 5. Heat flux–time profile in DC at 150°C (scale on the left) and temperature in the centre of the sample–time history (scale on the right).
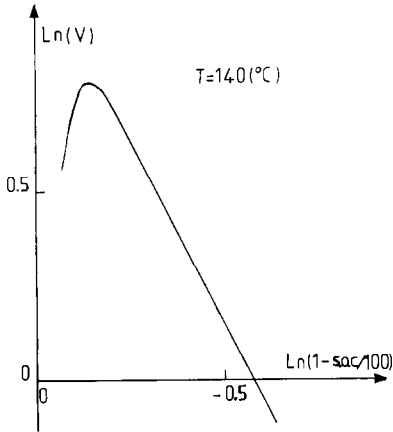
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Fig. 6. Ln (rate of reaction) as a function of ln $(1 - SOC/100)$ at $140\,°C$.

be drawn from these curves: there is a temperature increase in the sample during the reaction, especially at the centre of the sample; the temperature–time history passes through a maximum, which is attained at the same time as the maximum of the heat flux; and the higher the temperature of the calorimeter, the higher the increase in temperature at the centre of the resin.

Determination of the kinetic parameters from DC experiments

The kinetic parameters of the reaction have been determined from the heat flux–time histories at the three temperatures ranging from 140 to $160\,°C$.

The rate of reaction (in logarithmic form) has been expressed as a function of the remaining heat to be evolved at the lower temperature
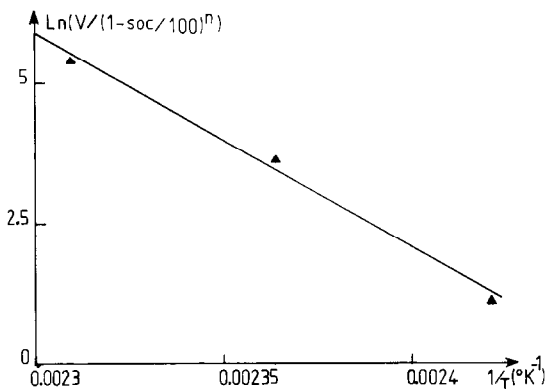

Fig. 7. Ln (rate of reaction) as a function of $1/T$ (K).

TABLE 2

Kinetic parameters of the reaction

	n	K_0 (s^{-1})	E (cal mol^{-1})
Calculated by DSC	1.56	2×10^{23}	50 018
Calculated by DC	2.1	3.6×10^{40}	76 000

(140°C) (Fig. 6). According to eqn. (4) describing the rate of reaction, the order of the reaction is equal to the slope. Following eqn. (4), the values of $\ln [V/(1 - SOC/100)^n]$ have been plotted as a function of the reciprocal temperature (Fig. 7). From the straight line obtained, the energy of activation (proportional to the slope) is calculated, as well as the rate constant K_0. The values of the kinetic parameters calculated in this way have been listed in Table 2. As shown in Table 2, the kinetic parameters obtained from DC experiments are quite different from the values obtained by DSC with the same resin. There are a number of reasons for this, one of which is clear from the temperature–time histories of the sample during the cure in DC mode. As shown in Figs. 3–5, the temperature selected for the calorimeter significantly affects the temperature increase of the sample.

CONCLUSIONS

The aim of this research has been to provide new ideas on how to obtain better values for the kinetic parameters of the reaction. From this study, some conclusions have been drawn about the size of the sample and the mode chosen for the calorimetry.

In spite of some inconveniences (especially the longer time involved), calorimeters with large samples are more useful than those with small samples because the quality of contact between the sample and holder as well as between the holder and calorimeter is higher in case of large samples, and because a large sample is more representative of the homogeneity of a large batch, this fact being very important in the case of composite materials.

The process developed in the sample is not simple because the heat evolved from the reaction is superimposed on the conductive heat transfer through the system. In the DC mode, strong heating occurs after introduction of the sample into the calorimeter, and a high increase in temperature within the sample follows the development of the reaction. The higher the temperature of the calorimeter, the higher this increase in sample temperature. As a result, there is only a rather narrow window width over which meaningful data can be obtained for each material. In DSC experiments, a constant shift towards lower values has been observed for the temperature of

the sample during the heating period, and it is followed by an increase in the sample temperature during the reaction. These temperature differences can be reduced to some extent in DSC, as they are proportional to the value chosen for the heating rate.

In conclusion, it would appear that DSC is the better mode for calorimetry because the difference in temperature between sample and calorimeter can be reduced by selecting a low heating rate, and because the comparison of the calculated and experimental heat flux–temperature histories is a good way to test the validity of the kinetic parameters.

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