

VARIATION OF ENTHALPY AND KINETIC PARAMETERS OF THE CURE OF EPOXIDE RESIN WITH THE COMPOSITION OF THE BINARY SYSTEM

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Abstract—This paper deals with the important problem of the mixing of the two viscous components of epoxide resin. Because of this difficulty, some change in the distribution of the components may occur, with resulting disturbance in the process and heterogeneity in mechanical properties. Various compositions have been tested by using calorimetry working in the scanning mode. Large samples of 150 mg allow one to avoid the possibility of having poor dispersion of components as occurs in very small samples. In order to reduce the large temperature gradients developed in the sample, a low heating rate of 2°C/min has been chosen. The enthalpy of cure is found to depend largely on the composition of the resin, with a constant value around 330 J/g obtained when the components are within the range 110–70 and 70–110. Kinetic parameters also vary with the composition.

INTRODUCTION

It is nearly always difficult to obtain perfect mixtures particularly for solids, but also for liquids when they are highly viscous. As a result of the difficulty of mixing two viscous components, a wide distribution in these components may occur in some parts of the mixture. This problem is then responsible for disturbing the development of the process not only when it is conducted on an industrial scale, with the resulting troublesome change in mechanical properties of final products, but also when it is carried out on a very small scale, e.g. in samples used in calorimetry, these samples being of the order of a few mg.

In the same way, the distribution of the two components for epoxide resin (the resin and hardener) is of greater interest. It has some important effects on the mechanical properties of the product and also on the kinetics of the reaction and the enthalpy of cure.

The main purposes of this paper are to determine the variation in the parameters of the kinetics of the overall reaction of cure and the value of the enthalpy of this reaction, as a function of the composition of the binary mixture.

In the small samples used in DSC, it is necessary that all ingredients are well dispersed otherwise there is lack of reproducibility. Then, the question which always arises is how representative is a 2–5 mg sample, taken from a large batch, of the good dispersion of the components in the batch. As in calorimetry, studies on the reaction present specific problems both in sample handling and in obtaining reproducible results, we have used apparatus with rather large

samples of about 100–200 mg. However, one source of error results from heat transfer between the specimen and the reference cell [1, 2], which particularly applies for reactions of high enthalpy as in the case of epoxide resin. It has been clearly shown that the applied temperature is the set calorimeter temperature and not the temperature in the sample during the cure, because of the local heating due to the highly exothermic reaction and low heat conductivity and diffusivity through the sample [3–6]. Moreover, the large size of the sample is responsible for the development of high gradients of temperature through the sample, the highest temperature being found at the middle of the sample.

In order to reduce the difficulty caused by the high exothermicity of reaction and low heat diffusivity, and in spite of the resulting lower sensitivity for the heat flux [7], we have used the DSC technique in the scanning mode with a low heating rate.

THEORETICAL

The kinetics of the thermosetting reaction have been studied using various techniques, and more recently with DC or DSC [8, 9]. The study of the reaction kinetics of epoxy cure by means of DSC has been widely discussed [10–12].

The curing reaction of epoxy-amine systems was described for the first time [9] by means of the expression

$$\frac{d\alpha}{dt} = (k_1 + k_2 \cdot \alpha^m)(1 - \alpha)^n \quad (1)$$

giving the rate of reaction as a function of the degree

of cure α , k_1 and k_2 being kinetic constants varying with temperature according to the Arrhenius law. After this first attempt, this kinetic law has been widely used subsequently [8–12].

More recently, another kinetic expression giving results in good agreement with experiment, has been tested [4–7, 13]. The rate of heat production during cure is expressed as a function of the heat of reaction as follows:

$$\frac{1}{Q_\infty} \cdot \frac{dQ_t}{dt} = k_0 \left(1 - \frac{Q_t}{Q_\infty}\right)^n \cdot \exp\left(-\frac{E}{RT}\right) \quad (2)$$

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

In order to obtain the values of the frequency factor, k_0 , the order, n , and the activation energy, E , from experiments carried out in the scanning mode, we have used several methods [14, 15]. To ensure that these kinetic parameters are obtained with sufficient accuracy, dynamic thermograms have been simulated using these calculated parameters and compared with the experimental heat flux–time curves.

EXPERIMENTAL

Formulations used in this study consist of: (i) epoxide resin containing DGEBA (Lopox 200-CDF-Chimie); (ii) hardener (D. 2605 CDF-Chimie) containing a mixture of an anhydride of MeTHP and of an accelerator, at 0.75%, of the aromatic amine type (A 105-CDF-Chimie). Various compositions for this binary mixture, ranging from 20 to 160 parts (by weight) of the resin and 160 to 20 parts of the hardener (the total amount being 180 parts by weight in every case) have been prepared. The mixture is prepared by heating the resin to room temperature and adding the hardener with continuous stirring until a clear mixture is obtained. The mixture is then stored at about 5°C.

Techniques

The mixture warmed to room temperature is placed in a hermetically sealed iron–steel holder having 5.1 mm external diameter. The weight of the sample is about 150 mg. Heat flux measurements are made as a function of time and temperature with the DSC (DSC 111, Setarem, France) from 30° to 250°C, using a constant heating rate of 2°C/min.

After cooling the calorimeter and sample to 30°C, the calorimeter is heated again under the same conditions in order to obtain the baseline for heat flux–time curves.

Calculations

A microcomputer (Hewlett–Packard 86) coupled with the DSC stores the data (heat flux, time and temperature) at definite times. After the first run allowing calculation of the total enthalpy change, the following runs allow determination of the kinetic parameters by various methods. The last run allows the validity of these parameters to be tested by superimposing heat flux–time curves obtained by experiment and calculation.

RESULTS

Validity of the kinetic equation and parameters

As shown in Fig. 1, the heat flux–time curves obtained by experiment and calculation agree very well, proving the validity of the methods of calculation for kinetic parameters and justifying the use of such a simple kinetic equation with a constant energy of activation. In fact, it has been necessary to draw a third curve showing the difference between experimental and calculated heat flux as a function of time, in order to appreciate the difference between these data. Each of the following results has been tested in this way.

Kinetic parameters as a function of resin formulation

Different heat flux–time curves, obtained with the various formulations shown in Table 1, can be seen in Figs 2–4. More information is also given by the computer, as the value of the state of cure (expressed as the extent of heat evolved from the cure, in percent) for various temperatures.

For various compositions of the binary mixture, data are shown in Table 1, as the total enthalpy of cure (J/g), the energy of activation (J/mol), the frequency factor (sec^{-1}), the order, two numbers qualifying the maximum value of the heat flux (the temperature at which this maximum is obtained and the corresponding value of the state of cure) and a

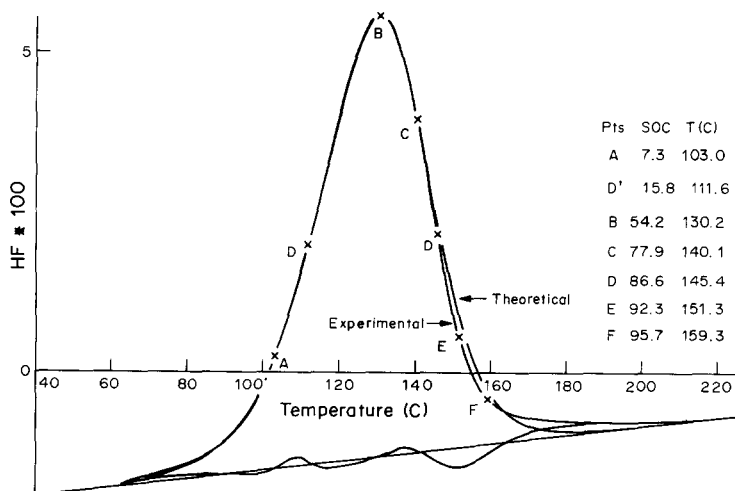


Fig. 1. Superimposition of heat flux–time curves: calculated and experimental (100 resin + 80 hardener in weight).

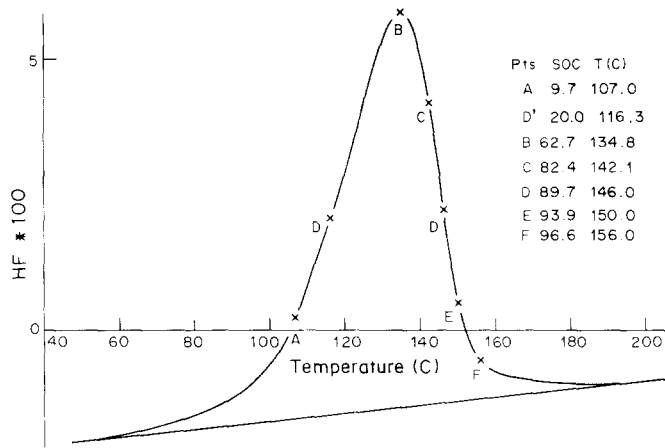


Fig. 2. Heat flux-time curves obtained with the composition: 110 resin + 70 hardener.

correlation factor. The correlation factor, obtained by dividing the maximum value of the calculated heat flux by the corresponding experimental value, is a measure of the quality of superimposition.

As shown by the value of the correlation factor, good agreement is obtained for formulations ranging

from 80 to 110 parts for the resin. For compositions below 60 and above 110, poor agreement is found.

A parameter of great interest is the total enthalpy of cure; its variation with the composition of the mixtures is shown in Fig. 5. The enthalpy of cure is nearly constant at about 330 J/g when the com-

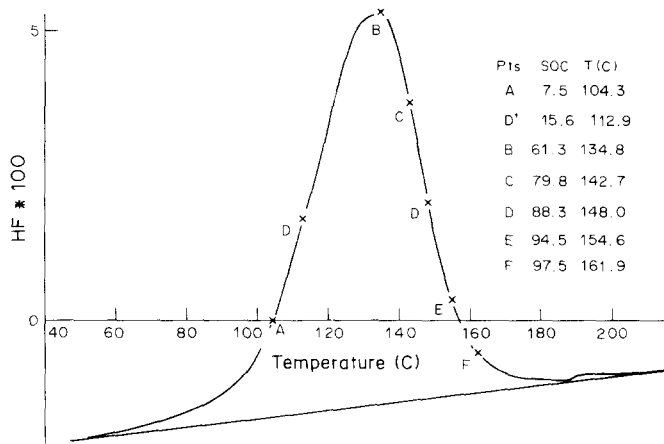


Fig. 3. Heat flux-time curves obtained with the composition: 90 resin + 90 hardener.

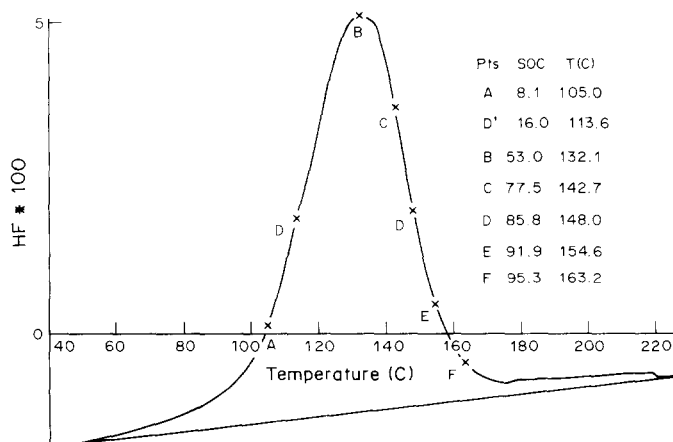


Fig. 4. Heat flux-time curves obtained with the composition: 80 resin + 100 hardener.

Table 1. Variation of enthalpy and kinetic parameters with the composition

Resin + hardener	Weight % hardener	Enthalpy (J/g)	E (J/mol)	$10^{11} \cdot K_0$ (sec)	n	T (°C)	HF _{max} SOC (%)	Correlation factor
20 160	89	87.8	135,850	5×10^3	1.5	137	58	0.91
60 120	66.6	255	133,760	6×10^3	1.6	132	56	0.91
80 100	55.5	323.5	115,786	17.5	1.5	132	53	1.00
90 90	50	333.5	114,281	12.3	1.5	134	61	0.98
100 80	44.5	334.8	113,445	11.5	1.5	130	54	0.99
110 70	39	313.5	106,172	0.8	1	134	62	0.98
160 20	11	100.3	104,500	0.5	0.75	136	70	0.94

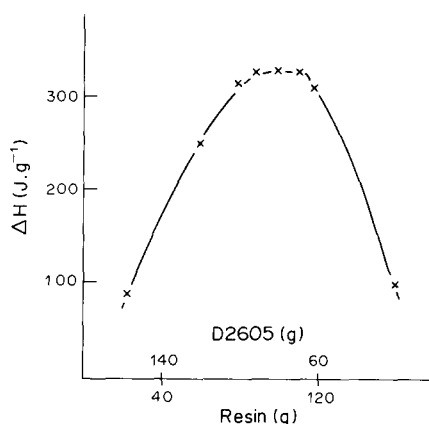


Fig. 5. Variation of the enthalpy of cure (per g/resin) as a function of the composition.

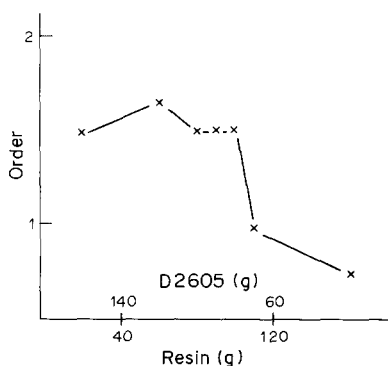


Fig. 6. Variation of the order in the kinetic expression as a function of the composition.

position ranges from 80 to 120 parts for the resin. The enthalpy decreases considerably when the composition is outside this range. The order, after being about constant at about 1.5, decreases to nearly 1 when the amount of the resin is increased (Fig. 6). The energy of activation increases regularly as the percentage of the hardener is increased.

In fact, after some previous studies [16–18] on the effect of the kinetic parameters on the position and shape of heat flux–time curves, we may draw the following conclusions:

(i) The value of the order of the overall reaction has no effect on the position of the heat flux–time curves, because it has no effect on the value of the reaction rate when the state of cure is below 50%. On the contrary, this parameter has a large effect on the shape of the tail of this curve, when the extent of cure exceeds 80% [17].

(ii) The parameters frequency factor and activation energy have a strong effect on the position of the heat flux–time curve [16–18]. Of course, too high a value for the activation energy causes an increase in the value of the frequency factor.

CONCLUSIONS

The heat evolved from the cure reaction in epoxide resin can be expressed by a single kinetic equation with an order and constant energy of activation: all the kinetic parameters have been determined with good accuracy. The validity of the equation and parameters has been established by superimposing the experimental heat flux–time curves with the corresponding curves calculated with the help of kinetic parameters obtained beforehand with various techniques.

The effects of the composition of the resin is found to be of great importance on the value of the enthalpy of cure and kinetic parameters. In fact, the enthalpy of cure is almost constant at 330 J/g of resin when its composition (expressed as weight percentage of hardener) is varied between 39 and 55. This point is of interest because it shows that a variation in the distribution of the components of about 10% has no real effect on the enthalpy of cure. Within the same range, the kinetic parameters remain about constant with an order of 1.5.

This study allows further insight on the important problem of the mixing of components during preparation of epoxide resin. However, the work is still in progress, because more precise information is needed in order to correlate the mechanical properties of the final materials with composition.

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