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A kinetic analysis of the curing reaction of an epoxy resin

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Abstract

The kinetics of a curing reaction under non-isothermal conditions using DSC is discussed. A simple, consistent method of kinetic analysis was applied. The method allows the correct determination of the most suitable kinetic model and the calculation of kinetic parameters. This method was used to study the kinetics of an epoxy resin based on diglycidyl ether of bisphenol A, cured by methyl tetrahydrophthalic anhydride with an accelerator. An activation energy of 73 kJ mol^{-1} was calculated and the autocatalytic kinetic model (Šesták–Berggren equation) was found to be the most covenient description of the studied curing process.

The isothermal curves calculated for the kinetic parameters determined in non-isothermal conditions are in good agreement with experimental curves when the curing temperature T_c is above the maximum glass-transition temperature of the system, $T_{g\infty} = 109$°C. The influence of the vitrification phenomenon is discussed when T_c is below $T_{g\infty}$. The temperature–time–transformation diagram of the studied epoxy system has been constructed and is discussed.

INTRODUCTION

The physical properties of a thermosetting system are dependent on the extent of cure, which depends on the curing conditions, and the time and temperature of cure. For this reason, the kinetic characterization of a curing reaction is important in order to obtain thermosets with controlled physical properties and for establishing optimum curing conditions.

Since the pioneering work of Fava [1], differential scanning calorimetry (DSC) has been found to be a useful method with which to study exothermic curing reactions [2,3]. The kinetic parameters of the curing

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reaction can be determined by isothermal methods. When the curing temperature T_c is well above the maximum glass-transition temperature of the cured resin $T_{g\infty}$, the isothermal curing can be carried out directly in the DSC calorimeter. By this method, both the rate of the reaction as well as the extent of curing are monitored simultaneously during the course of the reaction. When the heat flow evolved due to the exothermic reaction is too small to be measured by the calorimeter, or when $T_c < T_{g\infty}$, the method of residual heat of curing must be applied [1,2]. This is a rather time-consuming method but it gives useful data about the vitrification process which appears when the T_g of the system is equal to T_c.

The kinetic data can also be obtained using non-isothermal experiments. This method is very attractive because the kinetic data can be obtained in a relatively short period of time. Nevertheless, there are some complications in the mathematical analysis of the temperature integral which are inherent to the non-isothermal approach. The method which involves single or multiple dynamic temperature scans has been applied extensively in the study of the curing reactions of thermosets [1–11].

Certain differences between the kinetic data from isothermal and non-isothermal measurements have been observed. Prime [4] has found that for an epoxy–polyamide system, the apparent activation energy and pre-exponential factor determined from non-isothermal experiments were considerably higher than the isothermal values. Provder et al. [5] found similar discrepancies in an epoxy–amine system. Some authors [6,7] have proposed general methods of relating non-isothermal kinetic data with isothermal data.

However, rather good agreement between both isothermal and non-isothermal measurements has been observed in other polymeric systems. Ng and Manas-Zloczower [8] have proposed a mechanistic model for the curing of an unsaturated polyester system. The application of this model to the dynamic DSC measurements provide reliable kinetic data over a broad temperature range. Other authors [9–11] have proposed phenomenological models taking into account the vitrification process. In the system methyl methacrylate–ethylene glycoldimethacrylate, Gonzalez-Romero and Casillas [9] found that the kinetic parameters from isothermal and dynamic experiments are relatively close. The model proposed by Kenny et al. [10,11] is able to describe incomplete reaction in isothermal curing and the heating rate dependence of dynamic scans in epoxy matrices. The aim of this work is to obtain the kinetic parameters of the curing reaction of an epoxy–anhydride system from non-isothermal DSC measurements, applying a simple, consistent method of kinetic analysis [12]. The kinetic results obtained from non-isothermal data allow us to calculate theoretical isothermal curves which show very good agreement with the experimental curves obtained at curing temperatures above $T_{g\infty}$.

THEORY

The basic rate equation in kinetic analysis is

$$(\mathrm{d}\alpha/\mathrm{d}t) = k(T)f(\alpha) \tag{1}$$

where $\mathrm{d}\alpha/\mathrm{d}t$ is the rate of conversion, $k(T)$ is a reaction rate constant and $f(\alpha)$ is some function of the fractional conversion α. The rate constant $k(T)$ is dependent on the temperature and is assumed to be of the Arrhenius form

$$k(T) = A\exp(-E/RT) \tag{2}$$

where A is the pre-exponential factor and E is the apparent activation energy. It is assumed that the rate of conversion is directly proportional to the rate of heat flow ϕ generated in the curing reaction

$$(\mathrm{d}\alpha/\mathrm{d}t) = \frac{(\mathrm{d}H/\mathrm{d}t)}{\Delta H} = \frac{\phi}{\Delta H} \tag{3}$$

ΔH being the enthalpy of the curing reaction. Combining eqns. (1)–(3), the heat flow rate ϕ measured by differential scanning calorimetry is controlled by the kinetics of the curing process of the epoxy–anhydride system and can be described by the equation [13]

$$\phi = \Delta HA\,\mathrm{e}^{-x}f(\alpha) \tag{4}$$

where $x = E/RT$ is the reduced activation energy. The function $f(\alpha)$ represents the mathematical expression of the phenomenological kinetic model. The kinetic models most frequently cited in the literature [13] are summarized in Table 1. The two-parameter Šesták–Berggren model [26] (also called the autocatalytic model [2]) and the reaction order model are those that are mostly applied in curing reactions.

The aim of the kinetic analysis of DSC data is to find the kinetic model which gives the best description of the studied process and allows the behaviour of the system to be predicted under selected thermal conditions.

TABLE 1

The kinetic models

Model	Symbol	$f(\alpha)$
Šesták–Berggren	SB(m, n)	$\alpha^m(1-\alpha)^n$
Johnson–Mehl–Avrami	JMA(n)	$n(1-\alpha)[-\ln(1-\alpha)]^{1-1/n}$
Reaction order	RO(n)	$(1-\alpha)^n$
2D-diffusion	D2	$1/[-\ln(1-\alpha)]$
Jander eqn.	D3	$\frac{3}{2}(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}$
Ginstling–Brounshtein	D4	$\frac{3}{2}[(1-\alpha)^{-1/3}-1]^{-1}$

During the non-isothermal DSC experiment, the temperature rises at a constant rate β. In this case, after integration of eqn. (4) we obtain the integral kinetic equation

$$g(\alpha) = \int_0^\alpha \frac{\mathrm{d}\alpha}{f(\alpha)} = \frac{AE}{\beta R}\mathrm{e}^{-x}\left[\frac{\pi(x)}{x}\right] \tag{5}$$

where $\pi(x)$ is an approximation of the temperature integral [13] which has to be introduced because the exponential term cannot be integrated analytically. There are many approximate expressions of the $\pi(x)$ function in the literature. According to our experience, the 4th rational expression of Senum and Yang [14] gives sufficiently accurate results

$$\pi(x) = \frac{x^3 + 18x^2 + 88x + 96}{x^4 + 20x^3 + 120x^2 + 240x + 120} \tag{6}$$

It is important to stress that the reduced activation energy and the pre-exponential factor in eqns. (4) and (5) are mutually correlated [12, 15, 16]. Therefore, methods of kinetic analysis using multiple linear regression or even non-linear regression algorithms can hardly give reliable kinetic results. This problem can be solved, however, if the activation energy is known. The calculation of activation energy is based on a multiple-scan method in which several measurements at different heating rates are needed. A very simple method [17] for calculating the activation energy follows from the logarithmic form of eqn. (4)

$$\ln \phi = \ln[\Delta H A f(\alpha)] - E/RT \tag{7}$$

The slope of the ln ϕ versus $1/T$ dependence for the same value of α at any heating rate gives the value of the activation energy E. This procedure, called the isoconversional method, can be repeated for various values of α and, in this way, it provides a simple check for the invariance of E with respect to α which is a basic assumption for the validity of eqn. (4).

Once the activation energy has been determined, it is possible to find the kinetic model which best describes the non-isothermal DSC data. It is useful to define two following functions for this purpose [12, 18, 19]

$$y(\alpha) = \phi\,\mathrm{e}^x \tag{8}$$

$$z(\alpha) = \pi(x)\phi T/\beta \tag{9}$$

It is evident that if the activation energy is known, both the $y(\alpha)$ and $z(\alpha)$ functions can be obtained from experimental DSC data using eqns. (8) and (9). Comparing eqns. (4) and (8), we obtain another expression for the $y(\alpha)$ function

$$y(\alpha) = \Delta H A f(\alpha) \tag{10}$$

Therefore, this function is proportional to the kinetic model $f(\alpha)$ and it can easily be used for the kinetic model determination [12, 19]. The maximum α_{M} of the $y(\alpha)$ function is a very important parameter in this respect. It

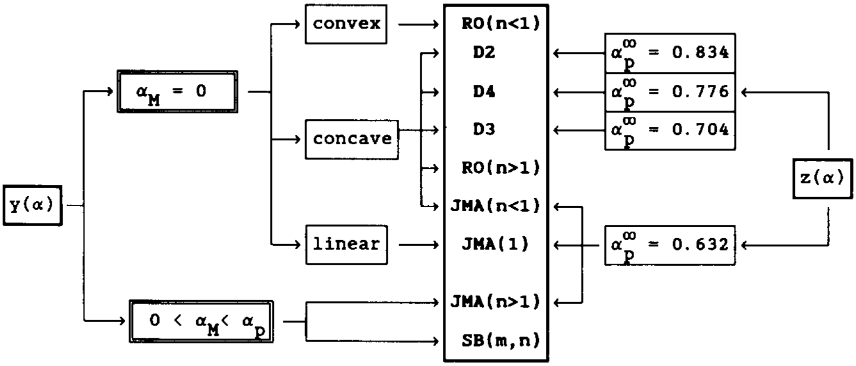

Fig. 1. Schematic diagram of the kinetic model determination.

should be stressed, however, that the shape of the $y(\alpha)$ function is strongly affected by E. Hence, a reliable value of the activation energy is vital for meaningful kinetic analysis.

Combining eqns. (4), (5) and (9) yields the following expression for the $z(\alpha)$ function

$$z(\alpha) = \Delta H g(\alpha) f(\alpha) \tag{11}$$

It is easy to demonstrate [12] that the $z(\alpha)$ function has a maximum at α_p^∞ for any kinetic model. This parameter has a characteristic value for a given kinetic model and it is practically independent of the value of the activation energy.

Both α_M and α_p^∞ are extremely important parameters for the determination of the most suitable $f(\alpha)$ function. Their combination can suggest the choice of the kinetic model [12] as shown by the scheme in Fig. 1. Once the kinetic model has been determined the kinetic parameters, such as the pre-exponential factor and the kinetic exponents can easily be calculated by the methods described in ref. 12.

EXPERIMENTAL

A commercial epoxy resin based on diglycidyl ether of bisphenol A (CIBA GEIGY Araldite CY225) with an epoxy equivalent of 188 g equiv^{-1} and a Hoepler viscosity of 11540 mPas was used in this study. A hardener derived from methyl tetrahydrophthalic anhydride with an accelerator (CIBA GEIGY HY225) was used to cure the resin. The resin and hardener were mixed in a weight ratio of 10:8. The mixture was stirred at room temperature for 20 min and then degassed in a vacuum chamber at room temperature for 15 min. Samples of about 10 mg were encapsulated in aluminium DSC pans and they were measured using a Mettler TA4000 thermoanalyser coupled with a low-temperature DSC30 module. The instrument was previously calibrated with indium, lead and zinc standards.

Non-isothermal DSC curves were obtained with selected heating rates

TABLE 2

Enthalpy of isothermal curing and residual enthalpy

T_c/°C	$-\Delta H_{iso}$/J g^{-1}	$-\Delta H_{res}$/J g^{-1}
140	293	6
130	281	11
120	286	14

(2.5–20 K min^{-1}) in the range from −80°C to 280°C. A second DSC scan was performed at 10 K min^{-1} in order to measure the glass transition temperature of the fully cured epoxy resin under these conditions. The maximum glass transition temperature of the fully cured epoxy resin was $T_{g\infty} = 109$°C [20, 21].

Isothermal DSC curves at curing temperatures of 120–140°C were recorded directly in the calorimeter. The sample was placed in the DSC cell at ambient temperature and the temperature was increased at 80 K min^{-1} to the required curing temperature. After the isothermal curing measurements, the samples were scanned again at 10 K min^{-1} in order to obtain the residual heat of curing (ΔH_{res}) (see Table 2).

Isothermal curing analysis at temperatures below 120°C was performed by the method of residual enthalpy because of the very low level of the heat flow which does not allow accurate results to be obtained. Samples were enclosed in aluminium DSC pans and placed in a thermostatic bath at a curing temperature T_c for different periods of time. These samples were scanned in the calorimeter at 10 K min^{-1} and the residual enthalpy of curing ΔH_{res} was measured. The extent of the curing process was then calculated using the equation

$$\alpha = \frac{\Delta H_T - \Delta H_{res}}{\Delta H_T}$$

where ΔH_T is the total enthalpy of curing corresponding to the "as mixed" sample without curing treatment ($-\Delta H_T = 298$ J g^{-1}). This procedure is described in a previous paper [20].

The kinetic analysis of the DSC data and all calculations were performed by the TA-SYSTEM software package [12].

RESULTS AND DISCUSSION

Figure 2 shows the DSC curves of uncured resin measured at four different heating rates. The average enthalpy of curing was determined as $-\Delta H = 298$ J g^{-1}. These non-isothermal curves were used for kinetic calculations. The values of the activation energy calculated by the isoconversional method for different values of the degree of curing are

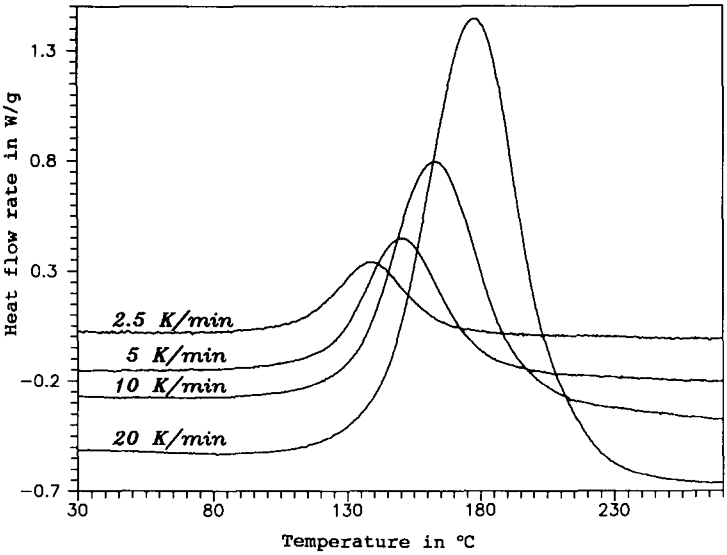

Fig. 2. DSC curves of samples cured at different scanning rates.

plotted in Fig. 3. The value of the activation energy is practically constant in the interval $0.4 < \alpha < 0.8$. This mean value of the activation energy, $E = 73\ \mathrm{kJ\,mol^{-1}}$ (shown by the broken line), was used for subsequent kinetic calculations. As evident from the error bars, the most accurate results are obtained around the maximum of the DSC peak ($\alpha_p = 0.51 \pm 0.01$). However, the peak tails, i.e. $\alpha < 0.2$ and $\alpha > 0.8$, lead to

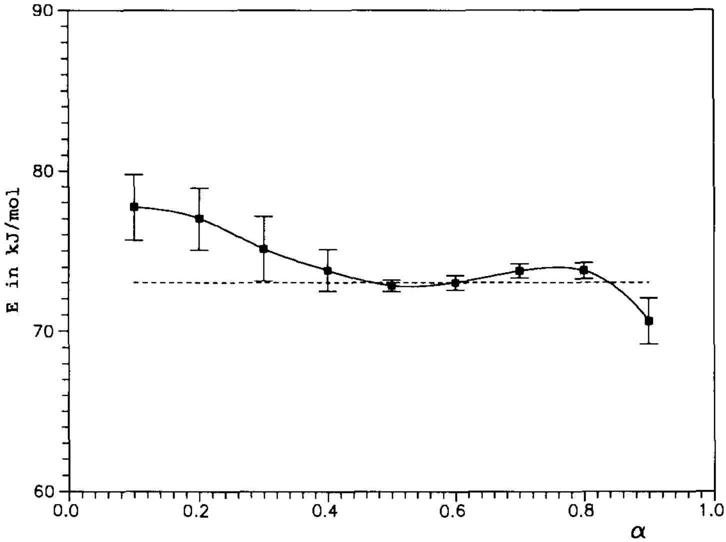

Fig. 3. The values of the activation energy calculated by the isoconversional method at various values of α.

higher error levels in the calculated activation energy. The calculated activation energy agrees with values for the epoxy–anhydride system reported by Fava [1] (74.6 kJ mol^{-1}) and Zukas [22] (75.6 kJ mol^{-1}).

The DSC data shown in Fig. 2 were converted to $y(\alpha)$ and $z(\alpha)$ functions using eqns. (8) and (9). These functions normalized within the $\langle 0, 1\rangle$ interval are plotted in Fig. 4 for different heating rates (points). For better clarity, not all the experimental data points are included in this figure. It is evident

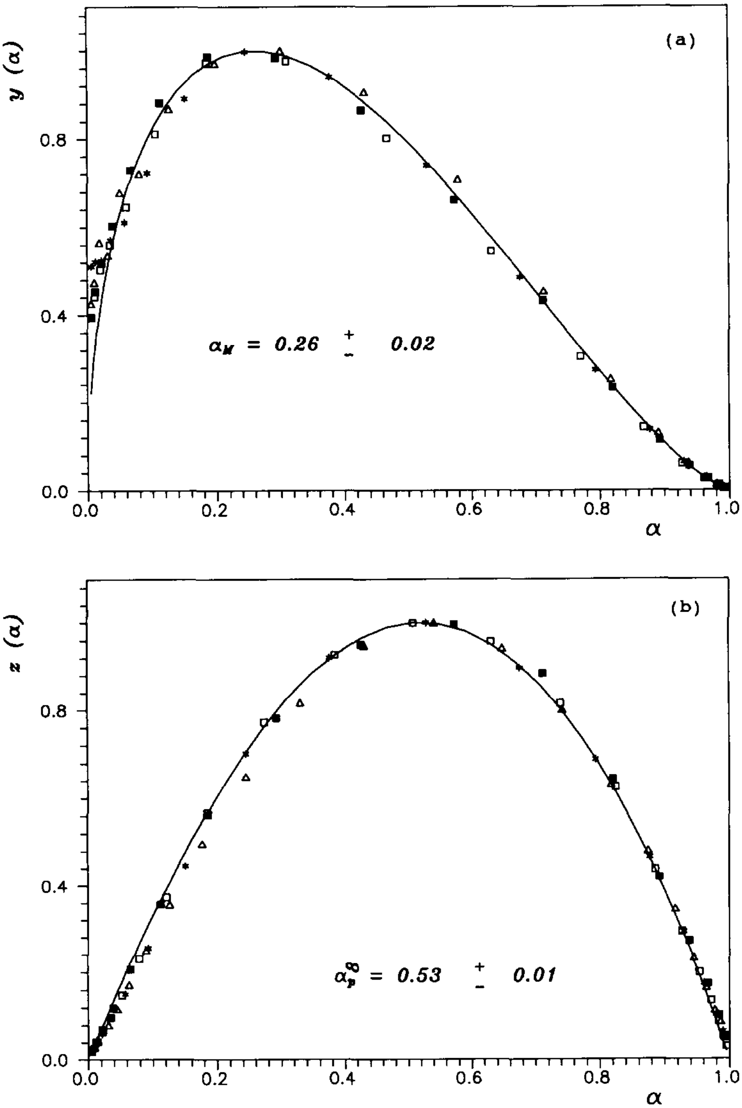

Fig. 4. (a) Normalized $y(\alpha)$ function. (b) Normalized $z(\alpha)$ function. The heating rates are shown by various points: △, 2.5; *, 5; □, 10; and ■, 20 K min^{-1}. The points were calculated by eqns. (8) and (9), and the full lines by eqns. (10) and (11).

TABLE 3

The kinetic parameters for curing of the epoxy resin

β/K min^{-1}	m	n	ln[A/(1/s)]
2.5	0.54	1.44	16.1
5	0.50	1.42	15.9
10	0.47	1.44	15.9
20	0.43	1.38	15.8
Mean	0.49	1.42	15.9

that all these functions are independent of the heating rate and give well-defined maxima: $\alpha_M = 0.26 \pm 0.02$ and $\alpha_p^{\infty} = 0.53 \pm 0.01$.

Comparing these results with the scheme in Fig. 1, the most suitable $f(\alpha)$ function corresponds to the autocatalytic two-parameter SB(m, n) model. Table 3 summarizes the kinetic parameters calculated for the kinetic model proposed. It can be seen that the variation of any kinetic parameter with heating rate does not exceed 10% of the average value.

Experimental DSC data (points) and curves (full lines) calculated using the kinetic parameters corresponding to each heating rate (see Table 3) are compared in Fig. 5. It is obvious that the two-parameter SB(m, n) model gives a good description of the curing process. The consistency of the model proposed can be checked by comparing the $y(\alpha)$ and $z(\alpha)$ functions calculated by direct transformation of the experimental data (points) with

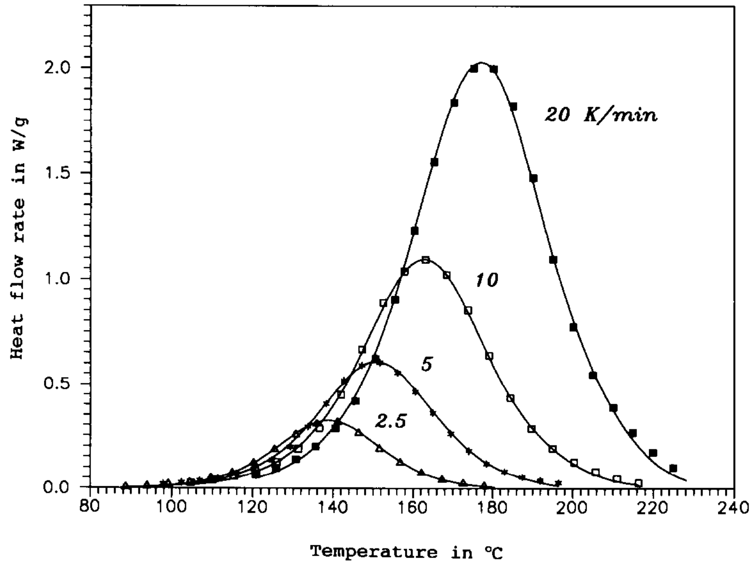

Fig. 5. Experimental (points) and calculated (full lines) DSC peaks corresponding to the curing process at various heating rates. The symbols used are as in Fig. 4.

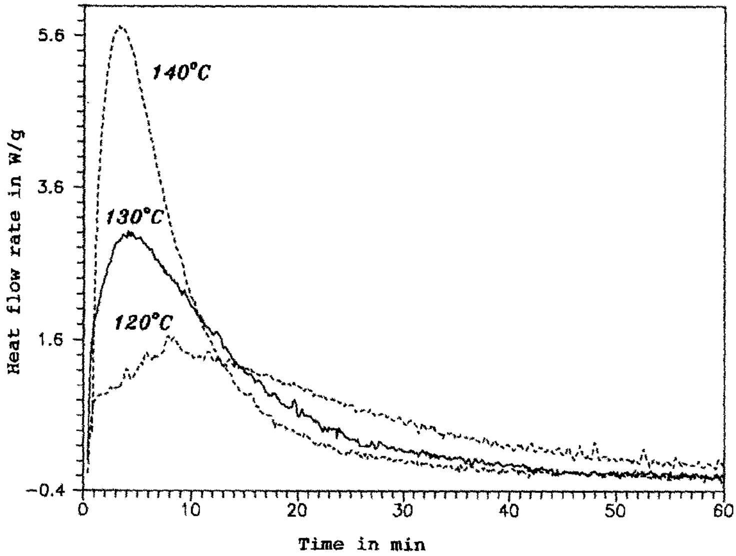

Fig. 6. Isothermal curing of the epoxy resin.

those calculated using eqns. (10) and (11) (full lines) for the average value of the kinetic parameters, as shown in Fig. 4.

It is interesting to compare the kinetic results obtained from non-isothermal data and isothermal experiments. Figure 6 shows typical isothermal DSC curves measured at isothermal curing temperatures T_c of 120, 130 and 140°C. These curves can easily be converted to α–t dependences as shown in Fig. 7 (points). After integration of eqn. (4) in isothermal conditions, the following expression is obtained

$$t = \frac{1}{A} g(\alpha)\, e^{x} \tag{12}$$

Taking the average kinetic parameters corresponding to non-isothermal data, we can calculate theoretical time–conversion curves because both A and $x = E/RT_c$ are constants. These calculated α–t curves are shown in Fig. 7 by full lines. It can be seen that the experimental and calculated curves are practically identical. Therefore it seems that for $120 \leq T_c \leq 140$°C where the kinetics of the curing process is controlled purely by chemical reaction, both isothermal and non-isothermal data as well as the corresponding kinetic parameters have the same relevancy.

The problem becomes more complicated at lower temperatures. When the isothermal curing temperature T_c is lower than the maximum glass transition temperature $T_{g\infty}$ which is about 109°C, the curing progresses through two different stages. The first is fully controlled by the chemical reactivity of the groups; the curing reaction develops in the liquid state and the T_g is lower than T_c. The reaction progresses at a rate depending on T_c

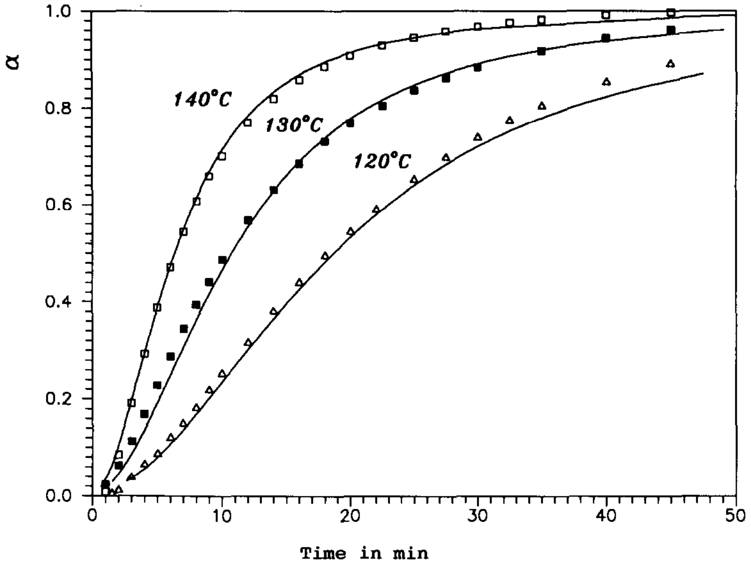

Fig. 7. Comparison between the experimental and calculated time–transformation curves. The points corresponds to the experimental data shown in Fig. 6. The full lines were calculated using the average kinetic parameters obtained from non-isothermal DSC data (see Table 3).

until the T_g of the system equals T_c. On reaching this point, the second stage of curing starts. The system vitrifies and the reaction rate decreases considerably until the reaction becomes practically frozen due to the fact that the mobility of the reacting groups becomes very restricted.

These two stages are evident in Fig. 8 where the isothermal α–t curves are shown for temperatures lower than 120°C. These isothermal data (points) cannot be measured directly as shown above for 120, 130 and 140°C because of the very low heat flow rate and, therefore, they have been constructed by the method of residual enthalpy (see Experimental). There is relatively good agreement between experimental points and predicted isotherms (the full lines were calculated using the average kinetic parameters given in Table 3) for low values of α. However, later the system reaches the glassy state and the kinetics becomes controlled by diffusion [20, 23–25]. The slow segmental motions are the only permitted ones and the measured α–t curves differ from the predicted curves. The extremely high viscosity of the system prevents full conversion of the chemical reaction and the degree of conversion tends to have a practically constant limiting value α_∞, even for very large time scales.

This area of restricted mobility where the vitrification occurs is also shown in the time–temperature–transformation (TTT) diagram in Fig. 9. This diagram was calculated using the average kinetic parameters (full lines) for $\alpha = 0.03$, 0.3, 0.6, 0.9, 0.99. The limiting values for T_g cor-

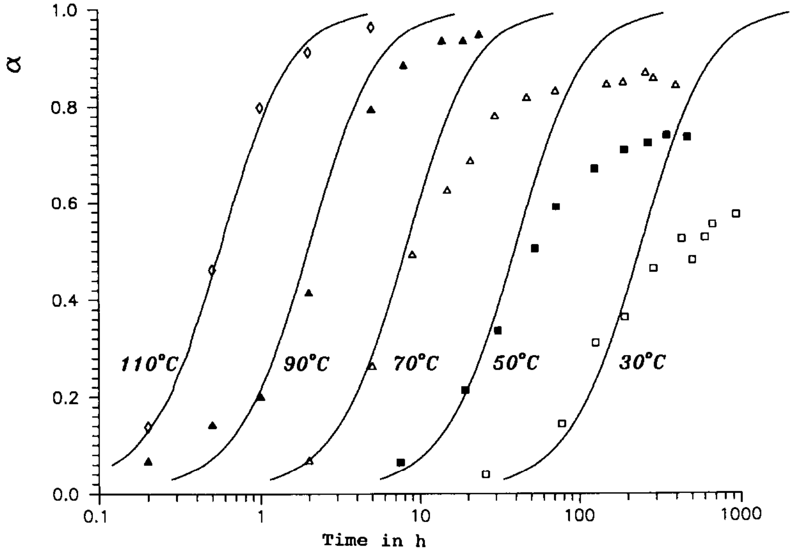

Fig. 8. Comparison between the experimental and calculated time–transformation curves. The points were determined from the residual enthalpy of partially cured resins. The full lines were calculated using the average kinetic parameters summarized in Table 3.

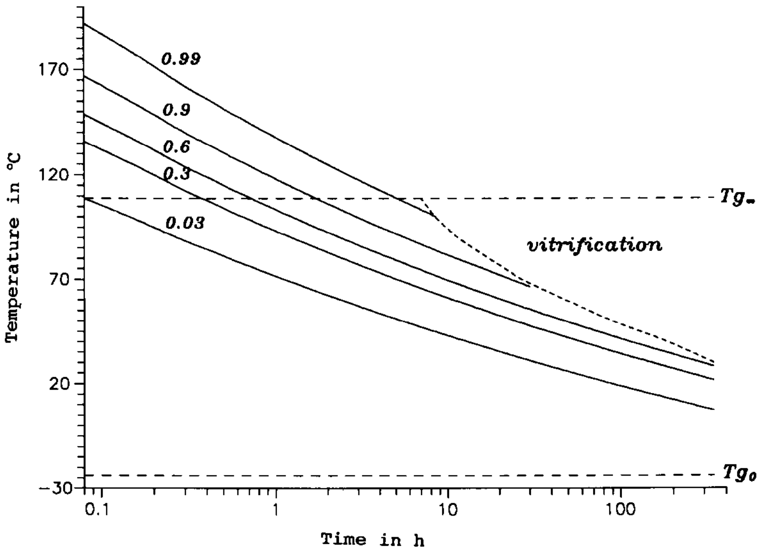

Fig. 9. Time–temperature–transformation diagram calculated for the average kinetic parameters (full lines $\alpha = 0.03$, 0.3, 0.6, 0.9, 0.99). The broken lines show the T_{g0} and $T_{g\infty}$. The vitrification region where the curing reaction is frozen by the dotted line.

responding to the uncured (T_{g0}) and fully cured ($T_{g\infty}$) resin are shown by broken lines. The T_g of a partially cured resin is confined to the range between these limiting values. If the curing temperature is lower than $T_{g\infty}$ then the system vitrifies after the vitrification time has elapsed. This vitrification time depends on the curing temperature [20] and it is shown by the dotted line.

CONCLUSION

A study of the kinetic characterization of an epoxy–anhydride system using non-isothermal DSC data is presented. Several measurements at various heating rates provide a determination of the activation energy and a simple, reliable method of kinetic analysis [12] enables us to select the most convenient model for the curing reaction.

It was established that the curing reaction of diglycidyl ether of bisphenol A with methylterahydrophthalic anhydride containing an accelerator, can be described by the two-parameter autocatalytic model (Šesták–Berggren equation).

The kinetic parameters obtained allow us to calculate theoretical isothermal curves showing a very good agreement with the experimental data obtained at curing temperatures above the maximum glass transition temperature of the system, $T_{g\infty} = 109°C$. If the curing temperature is lower than $T_{g\infty}$, then the system vitrifies after the vitrification time which depends on the curing temperature T_c [20]. When the vitrification time is reached, the kinetics of the curing reaction becomes controlled by diffusion and, as expected, a deviation is observed between the calculated and experimental α–t curves. A more complex model taking into account the vitrification phenomenon must be developed in order to be applied over the entire course of the curing reaction.

The calculated kinetic parameters also allow the construction of the TTT diagram which summarizes the behaviour of the epoxy–anhydride system during its isothermal curing.

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