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Thermochimica Acta 296 (1997) 155–159

thermochimica acta

Typical sources of error in the kinetic analysis of models with pre-equilibria: DSC investigations of epoxide–amine curing reactions

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Received 19 December 1996; received in revised form 24 February 1997; accepted 25 February 1997

Abstract

Reversible steps are included in many reaction models. If the intermediate reaches an equilibrium with the reactants, the kinetic evaluation may be simplified by using the corresponding equilibrium constant. Then, the adequate modelling of the reaction is based on the equilibrium concentrations of all participants of such a pre-equilibrium. Using DSC data for the investigation of kinetic problems, the concentrations are frequently replaced by the degrees of conversion (reaction). The formal use of degrees of conversion instead of concentrations results in incorrect kinetic equations. A typical example is the overall equation for the description of the epoxide–amine curing reaction. Another serious source of error is the unknown degree of conversion together with the unknown heat-flow rate at the apparent ending of the reaction. The resulting difficulties can partially be overcome, if the parameters of the complete set of differential equations are determined by multivariate nonlinear regression. © 1997 Elsevier Science B.V.

Keywords: Curing; DSC; Epoxy; Kinetics

1. Introduction

The polyaddition reaction of epoxides and amines is still intensively studied. The most used experimental technique is DSC. The model of reaction commonly employed was originally derived by Smith [1] and later on by Horie [2]. Especially in DSC papers, the overall kinetic law for an equimolar mixture of epoxide and amine is frequently written as

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha) \cdot (1 - \alpha)^2 \qquad (1)$$

where α is the degree of conversion or the fractional extent of the reaction at time t and k_1 and k_2 are overall rate constants for catalysis and autocatalysis. Using Eq. (1), only the first stage of the polyaddition reaction ($\alpha \leq 0.6$, degree of polymerization ≈ 1) can be described successfully. The evaluation of experimental data has shown that the relatively simple model of Smith must be completed by additional steps. Details may be found in numerous papers. But many investigators try to retain the simple form of the overall rate law, Eq. (1). The most popular modification is the introduction of n and m as empirical fitting parameters [3–5]:

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m) \cdot (1 - \alpha)^n \qquad (2)$$

The possible change from chemical control at low extent of the reaction to diffusion control in the later

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PII S0040-6031(97)00113-5

stages [6–8] is unimportant in regard to the aim of this paper. However, it is easy to show that Eq. (1) is by no means the correct equation, which follows from the Smith mechanism for epoxide curing reactions. Therefore, the failure of Eq. (1) is not necessarily caused by the failure of the underlying mechanism.

2. Results and discussion

For the sake of simplicity let us restrict ourselves to the curing of a stoichiometric (1 : 1) mixture of a bifunctional epoxide (e.g. bisphenol-A-diglycidylether, DGEBA) and a bifunctional amine (e.g. aniline). High-molecular, linear products ($M_n > 20\,000$) are then formed during the solvent-free polyaddition reaction. Let us neglect the different reactivities of primary and secondary amine hydrogens. Further, let us assume that the Smith mechanism (Fig. 1) is strictly valid. If the rate determining step is the formation of the termolecular transition state, then the reaction scheme is given by the Eqs. (3)–(5):

$$\mathrm{E} + \mathrm{HX} \overset{K}{\leftrightarrow} \mathrm{E} \cdots \mathrm{HX} \tag{3}$$

$$\mathrm{E} + \mathrm{A} \overset{k_1}{\rightarrow} \mathrm{PA} + \mathrm{HX} \tag{4}$$

$$\mathrm{E} \cdots \mathrm{HX} + \mathrm{A} \overset{k_2}{\rightarrow} \mathrm{PA} + 2\,\mathrm{HX} \tag{5}$$

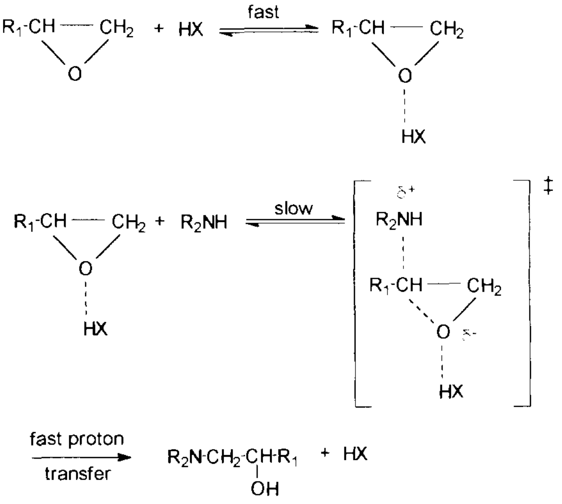

Fig. 1. The reaction scheme for the curing of epoxides by amines.

where E, A, PA and HX are the epoxide, the amine, the polyadduct and the catalytic species. The epoxide is activated in a pre-equilibrium, reaction (3), by the formation of a hydrogen bond between the oxygen of the oxirane ring and any proton donor. The subsequent reaction (5) is autocatalytic due to the OH-groups produced during the curing reaction, reactions (4) and (5). Very reactive amines can react with epoxides also in absence of proton donors during a noncatalytic reaction (4). Details of reaction (4) are unimportant in this context. If E, HX and E $\cdots$ HX are in equilibrium, the rate of formation of PA is given by

$$\begin{aligned}\frac{\mathrm{d}c_{\mathrm{PA}}}{\mathrm{d}t} &= k_1 c_{\mathrm{E,eq}} c_{\mathrm{A}} + k_2 c_{\mathrm{E\cdots HX,eq}} c_{\mathrm{A}} \\ &\equiv (k_1 + k_2 K c_{\mathrm{HX,eq}}) c_{\mathrm{E,eq}} c_{\mathrm{A}}\end{aligned} \tag{6}$$

where the subscript 'eq' implies the corresponding equilibrium concentrations of E, HX and E $\cdots$ HX. Plotting the so-called 'reduced reaction rate' $(\mathrm{d}c_{\mathrm{PA}}/\mathrm{d}t)/(c_{\mathrm{E,eq}}c_{\mathrm{A}})$ as function of $c_{\mathrm{HX,eq}}$ would give straight lines with the slope k_2K and the intercept k_2. If the experimental data result from methods which immediately provide the present (equilibrium) concentrations of all reactants, any misinterpretations are avoided.

By using the DSC data, we have a different situation. As a rule, the concentrations of the reactants are replaced by the degree of conversion α and the reaction rate is replaced by the normalized rate of conversion $\mathrm{d}\alpha/\mathrm{d}t$

$$\alpha = \frac{Q_t}{Q_\infty};\ \frac{\mathrm{d}\alpha}{\mathrm{d}t} = \frac{1}{Q_\infty}\frac{\mathrm{d}Q}{\mathrm{d}t} \tag{7}$$

where Q_∞ is the total peak area of the reaction peak and Q_t is the partial area up to the time t. The general validity of the Eq. (6) is completely lost by rewriting this equation as usual (Eq. (8)):

$$\begin{aligned}\frac{\mathrm{d}\alpha}{\mathrm{d}t} &= (k_1 c_0 + k_2 K c_0^2 \alpha)(1-\alpha)^2 \\ &\equiv (k_1' + k_2'\alpha)(1-\alpha)^2\end{aligned} \tag{8}$$

where c_0 is the initial concentration of the epoxide (amine).

The conversion degree α is always related to the total concentrations of the reactants, it never contains any information about the equilibrium concentrations of the reactants. Even if the epoxide–amine reaction could be described correctly by the foregoing model

Table 1
Assumed rate and equilibrium constants for the calculation of the heat-flow rate curves by means of Eqs. (6) and (8); $k_1 = 1 \times 10^{-5}\,\mathrm{s}^{-1}\,\mathrm{mol}^{-1}\,\mathrm{l}$, $k_2 = 1 \times 10^{-3}\,\mathrm{s}^{-1}\,\mathrm{mol}^{-1}\,\mathrm{l}$, $k_1' = 5.2 \times 10^{-5}\,\mathrm{s}^{-1}$, $c_A \equiv c_E = 5.2\,\mathrm{mol\,l}^{-1}$, $\Delta_r H = -110\,\mathrm{kJ\,mol}^{-1}$, $M_{PA} = 216.76\,\mathrm{g\,mol}^{-1}$

$K/(\mathrm{mol}^{-1}\,\mathrm{l})$	$k_2'/(\mathrm{s}^{-1})$
0.1	2.704×10^{-3}
0.7	1.890×10^{-2}
2.0	5.408×10^{-2}

(Eqs. (3)–(5)), the evaluation according to Eq. (8) gives erroneous results. The error is proportional to the value of the equilibrium constant K for the pre-equilibrium. Only in the case of very small equilibrium constants ($K \leq 0.1$), the usual plot of $(\mathrm{d}\alpha/\mathrm{d}t)/(1-\alpha)^2 = \mathrm{f}(\alpha)$ gives approximately straight lines.

To demonstrate this, we have calculated isothermal heat-flow rate curves, using the Eq. (6) and Eq. (8), for stoichiometric epoxide/amine-mixtures. All values, used for the calculation of the reaction isotherms, are given in the Table 1. Published equilibrium constants for the E $\cdots$ OH intermediate at 90°C are between $0.45\,\mathrm{l\,mol}^{-1}$ (phenyl glycidyl ether/cyclohexanol, [9]) and $1.05\,\mathrm{l\,mol}^{-1}$ (phenyl glycidyl ether/benzyl alcohol, [10]). In the DGEBA/aniline system, our own kinetic evaluations will be published later, we have found the mean equilibrium constant (in the (70–150)°C temperature range) of $0.7\,\mathrm{l\,mol}^{-1}$ between epoxide and hydroxylic groups. Fig. 2 clearly shows the dramatic differences of the calculated reaction isotherms. For the sake of clarity, only the curves for a very small ($K = 0.1\,\mathrm{l\,mol}^{-1}$) and a typical ($K = 0.7\,\mathrm{l\,mol}^{-1}$) equilibrium constants are shown. The higher the equilibrium constants, the greater the differences between the correct (Eq. (6)) and the incorrect calculation (Eq. (8)). Now, let us assume that the correctly calculated heat flow-rate curves correspond exactly to the experimental curves. In other words, the curing should be adequately and completely described by the Eqs. (3)–(5). Two cases are possible:

A. At any moment, the true degree of conversion and the true normalized heat-flow rates are actually known. This case is not fully realizable in practice. But even in this theoretical case the plot of $(\mathrm{d}\alpha/\mathrm{d}t)/(1-\alpha)^2$ (Fig. 3, solid lines) clearly gives no straight lines. The deviations from linearity increase proportionally to the assumed equilibrium constant. This emphasizes our above-mentioned statement: Plotting experimental data sets in such a way is no suitable test regarding the validity of the postulated reaction scheme, Eqs. (3)–(5).

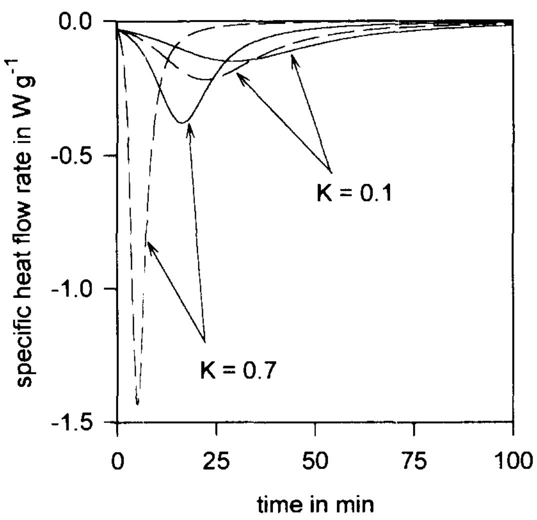

Fig. 2. Calculated correct (Eq. (6), solid lines) and incorrect (Eq. (8), broken lines) reaction isotherms for a small and a normal value of the equilibrium constant between epoxide and hydroxyls.

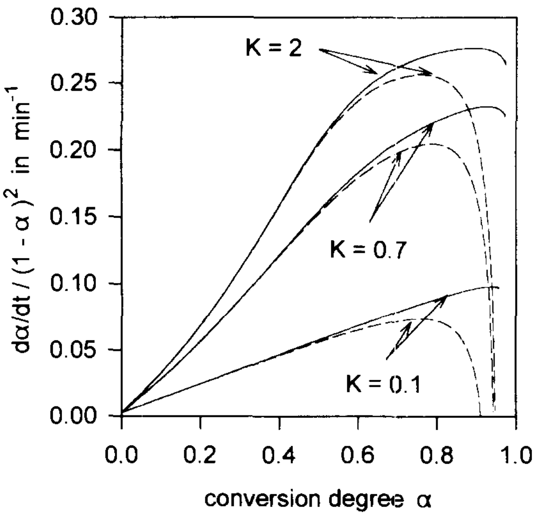

Fig. 3. The failure of the usual evaluation of isothermal DSC scans by plotting the reduced rate of reaction $(\mathrm{d}\alpha/\mathrm{d}t/(1-\alpha)^2$ as function of α; solid lines: use of theoretical data, calculated with Eq. (6); broken lines: modified data, which take into account a detection limit of the heat production.

B. Normally, the end of an isothermal scan is indicated by a constant heat-flow rate. Neither the degree of conversion nor the actual heat-flow rate at this time can be obtained from DSC experiments. Sometimes the true final α can be obtained from other methods, e.g. in the case of soluble polymers by determination of the number average molar mass. Two reasons may be responsible for a final $\alpha < 1$. The reaction stops due to diffusion hindrances or the heat-flow rate becomes smaller than the detection limit of the DSC. The first limitation can often be excluded by a sufficiently high isothermal temperature. The second limitation is critical in the case of very small heat production during the last stages of curing. According to Wies [11], a deviation from the baseline is a true signal, if its height is at least 2–5 times the noise. Very broad and slowly changing signals may be hard to identify due to additional long-range fluctuations of the baseline. Therefore, the assumption of a detection limit of at least 15 μW seems to be realistic. This corresponds to a heat production of 1.5 mW g^{-1} for typical sample masses of 10 mg. Table 2 shows, for the three assumed equilibrium constants, the reaction times, the true degrees of conversion after reaching the detection limit and, in the last column, the apparent degrees of conversion at this time, assuming $d\alpha/dt = 0$ for $dQ/dt < 15\ \mu W$. After subtracting the heat-flow rate of the detection limit from all calculated heat-flow rates, the resulting plot of $(d\alpha/dt)/(1-\alpha)^2$ is included in Fig. 3 (broken lines). As expected, the deviations from straight lines are markedly greater than in the first case. The differences between both plots become more marked with increasing degree of conversion due to the increasing error between true and apparent heat-flow rates.

Table 2
True and apparent degrees of conversion at the moment at which the heat production of the sample is lower than the assumed detection limit (15 μW) of the DSC (model calculations, using the parameters of Table 1)

$K/(\mathrm{mol}^{-1}\ \mathrm{l})$	$t/(\mathrm{min})$	α_{true}	$\alpha_{\mathrm{apparent}}$
0.1	271	0.959	0.908
0.7	169	0.973	0.941
2.0	153	0.975	0.946

Numerous published evaluations of curing reactions show plots of $(d\alpha/dt)/(1-\alpha)^2$, which are very similar to the broken lines of Fig. 2. Hence, it seems reasonable to assume that the failure of the postulated mechanism is at least partially an artefact, caused by the incorrect use of the degree of conversion and the experimental restrictions of recording very small heat productions. The replacement of Eq. (1) by Eq. (2) excludes these sources of error in a formal mathematical way!

We suggest a much better possibility to overcome the experimental difficulties. It is based on the determination of the optimized parameters for the assumed system of differential equations, using the different initial concentrations of all reactants and the technique of multivariate nonlinear regression (Mult-NLR) [12,13]. By means of the Mult-NLR several data sets, obtained at very different experimental conditions (heating rates, isothermal temperatures, stoichiometries), are described by the same kinetic model. The result is a global solution. On the other hand, the kinetic analysis of a single curve only provides a local solution. In the present example, we use different initial concentrations of the reactants. If the assumed model is valid, the corresponding influence on the heat-flow rate curves must be described by the same set of kinetic parameters. Even on the disadvantageous but realistic conditions of the case B, we obtain nearly correct rate and equilibrium constants. They are summarized in Table 3.

3. Conclusions

The results can be generalized. As usual, a reaction scheme with fast reversible steps (pre-equilibria) can be simplified by the use of the corresponding equilibrium constant instead of the rate constants for the forward and the reverse reaction. But the use of conversion degrees instead of concentrations always involves the risk of erroneous results and misinterpretations, and should generally be avoided. It follows that the greater the equilibrium constant K, the more unsuitable are these types of equations. Taking into account additional and nearly unavoidable experimental restrictions, the numeric solving of the complete assumed set of differential equations by nonlinear regression is always the convincing better variant

Table 3
Comparison of the true model parameters ($k_1 = 1 \times 10^{-5}\,s^{-1}\,mol^{-1}\,l$, $k_2 = 1 \times 10^{-3}\,s^{-1}\,mol^{-1}\,l$, $\Delta_r H = -110\,kJ\,mol^{-1}$) and the values, obtained by nonlinear regression of the Eqs. (3)–(5), on conditions of the realistic case B

Assumed/	Calculated			
K/(mol^{-1} l)	K/(mol^{-1} l)	$k_1/(s^{-1}\,mol^{-1}\,l)$	$k_2/(s^{-1}\,mol^{-1}\,l)$	$\Delta_r H/(kJ\,mol^{-1})$
0.1	0.120	1.10×10^{-5}	8.91×10−4	−107.35
0.7	0.703	1.13×10^{-5}	1.01×10^{-3}	−108.47
2.0	2.011	1.14×10^{-5}	1.01×10^{-3}	−108.73

on overall kinetic equations. For the kinetic modelling of the reaction scheme, the equilibrium constant should be determined as accurately as possible by independent measurements.

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