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ACTIVATION ENERGIES AND RATE CONSTANTS FOR AN EPOXY/CURE AGENT REACTION

Variation in peak exotherm temperature

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Abstract

From the peak reaction temperatures as a function of heating rate, the activation energies were obtained for a system consisting of an epoxy resin (Badge $n=0$) and a curing agent (isophorone diamine), using a Perkin Elmer DSC7 operated in the dynamic mode. At the same time, the Arrhenius law was used to calculate rate constants.

Keywords: activation energy, epoxy-amine reactions, rate constants

Introduction

Kinetic information can be extracted from dynamic experiments by means of various methods. One of these methods capitalizes on the variation in peak exotherm temperature with heating rate. This method is very useful for obtaining accurate measures of the activation energy and pre-exponential factor for all reactions. The study is based on the fact that the peak temperature varies in a predictable manner with the heating rate.

For an *n*th-order reaction, the rate of conversion is proportional to the concentration of material which has yet to react:

$$\frac{d\alpha}{dt} = kf(\alpha) \tag{1}$$

where k is a constant and α is the fractional concentration of reactant consumed after time t, and it is assumed that $f(\alpha)=(1-\alpha)^n$, with n unknown. In order to obtain data in the whole range of conversions and temperatures, trials must be

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performed on the value of n. However, the different physical parameters involved in the reaction may be known without an explicit knowledge of $f(\alpha)$.

From the Arrhenius law, $k=Ae^{-E/RT}$ and Eq. (1) becomes

$$\frac{d\alpha}{dt}=f(\alpha)Ae^{-E/RT} \tag{2}$$

where A, a pre-exponential factor, is a constant. If the sample temperature is changed by a controlled and constant heating rate Φ, the variation in the degree of conversion can be analysed as a function of temperature, this temperature being dependent on the time of heating. Therefore, the reaction rate may be written as follows

$$\frac{d\alpha}{dt}=\frac{d\alpha}{dT}\frac{dT}{dt} \tag{3}$$

The heating rate is defined as

$$\Phi=\frac{dT}{dt}$$

and Eq. [3] becomes

$$\frac{d\alpha}{dt}=\Phi\frac{d\alpha}{dT} \tag{4}$$

A combination of Eqs [2] and [4] leads to

$$\frac{d\alpha}{dt}=\Phi\frac{d\alpha}{dT}=f(\alpha)Ae^{-E/RT} \tag{5}$$

Assuming Φ=const. and rearranging in terms of the two variables:

$$\frac{d\alpha}{f(\alpha)}=\frac{A}{\Phi}e^{-E/RT}dT \tag{6}$$

Integration of this equation from an initial temperature T_o, corresponding to a degree of conversion α_o, to the peak temperature, where $\alpha=\alpha_p$, gives

$$\int_{\alpha_o}^{\alpha_p}\frac{d\alpha}{f(\alpha)}=\frac{A}{\Phi}\int_{T_o}^{T_p}e^{-E/RT}dT \tag{7}$$

If T_o is low, it may be reasonably assumed that $\alpha_o=0$, and considering that there is no reaction between 0 and T_o:

$$\int_{0}^{\alpha_{P}}\frac{\mathrm{d}\alpha}{f(\alpha)}=\frac{A}{\Phi}\int_{T_{o}}^{T_{P}}e^{-E/RT}\mathrm{d}T=\frac{A}{\Phi}\int_{0}^{T_{P}}e^{-E/RT}\mathrm{d}T\approx\frac{AE}{\Phi R}p\left(\frac{E}{RT}\right) \tag{8}$$

Values for $p(E/RT)$ were tabulated by Doyle [1].

For $20<E/RT<60$:

$$\log p\left(\frac{E}{RT}\right)\cong-2.315-0.4567\frac{E}{RT}$$

Prime [2] has observed that, for thermoset curing, the extent of reaction at the peak exotherm α_p is constant and independent of the heating rate. Therefore, the first integral in Eq. [8] is a constant, which leads to

$$E\approx-\frac{R}{0.4567}\frac{\Delta\log\Phi}{\Delta(1/T_p)} \tag{9}$$

The activation energy can be calculated from a plot of $\log\Phi$ *vs.* $1/T_p$.

A useful and accurate expression for the pre-exponential factor for *n*th-order reactions, which relates E, Φ and T_p, was derived by Kissinger [3]:

$$A=\frac{fEe^{E/RT_p}}{RT_p^2[n(1-\alpha_p)^{n-1}]} \tag{10}$$

Kissinger argued that $n(1-\alpha_p)^{n-1}\approx1$ and is independent of the rate of heating. Obviously, by definition, this is true for a first-order reaction. Prime [2] showed this quantity to be constant and only 2–4% greater than unity for an *n*th-order epoxy cure reaction, which permits us to write

$$A=\frac{fEe^{E/RT_P}}{RT_p^2} \tag{11}$$

Changing the sign and taking the logarithm of Eq. [11] yields

$$-\ln\left(\frac{f}{T_p^2}\right)=\frac{E}{RT_p}-\ln\left(\frac{AR}{E}\right) \tag{12}$$

which is the equation of a straight line if $y=-\ln(\Phi/T_p^2)$ and $x=1/T_p$. From a plot of y *vs.* x and fitting to a straight line, the activation energy E can be calculated from the slope and the pre-exponential factor from the intercept. From these data and the Arrhenius law, the rate constants may be derived.

An important contribution to the study of the Kissinger method, applied for determination of the activation energies of crystallization of metallic glasses and solid-state reactions in general, was made by Criado and Ortega [4]. However, we think that the method used here reasonably helps in a discussion of our results of the epoxy resin curing reaction.

Experimental

Materials

The epoxy resin systems used in this study consisted of a commercial diglycidyl ether of bisphenol A (Epikote 828 from S.P.E. Shell) and isophorone diamine, IPD (Hülls, Germany) as curing agent. The resin was purified by Gairesa (Spain) [5] and the IPD was used as supplied without further purification. The epoxide equivalent weight of the resin was 171 g/Eq and that of the IPD was 42.5 g/Eq, which gives a mixing ratio value of 100/24.85 for the stoichiometric relation.

IPD is worthy of study because it contains two different kinds of amine groups, as shown in Fig. 1, where (a) is an aliphatic group and (b) an alicyclic one. These groups exhibit different reactivities, the aliphatic group being more reactive than the alicyclic one [6, 7].

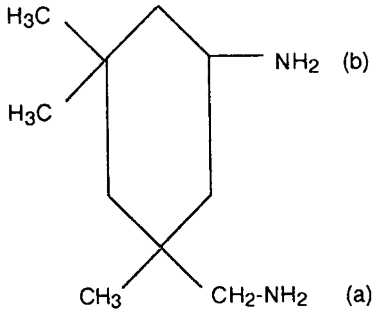

Fig. 1 Isophorone diamine

Techniques

Differential scanning calorimetry (DSC) was used. Calibration was performed by using the procedure given in the P.E. DSC7 Manual. Since the temperature range was between –25 and 250°C, an external cooling device (intercooler II supplied by P.E.) was used. All experiments were carried out under nitrogen (flow 40 ml $\min^{-1}$) and the mass of samples was 4–6 mg. To prevent early reactions, liquid sample (resin and IPD) and their different mixtures were kept at 10°C before being placed at once into the DSC.

All experiments were carried out at scanning rates (Φ) of 2, 5, 10, 15 or 30 K $\min^{-1}$.

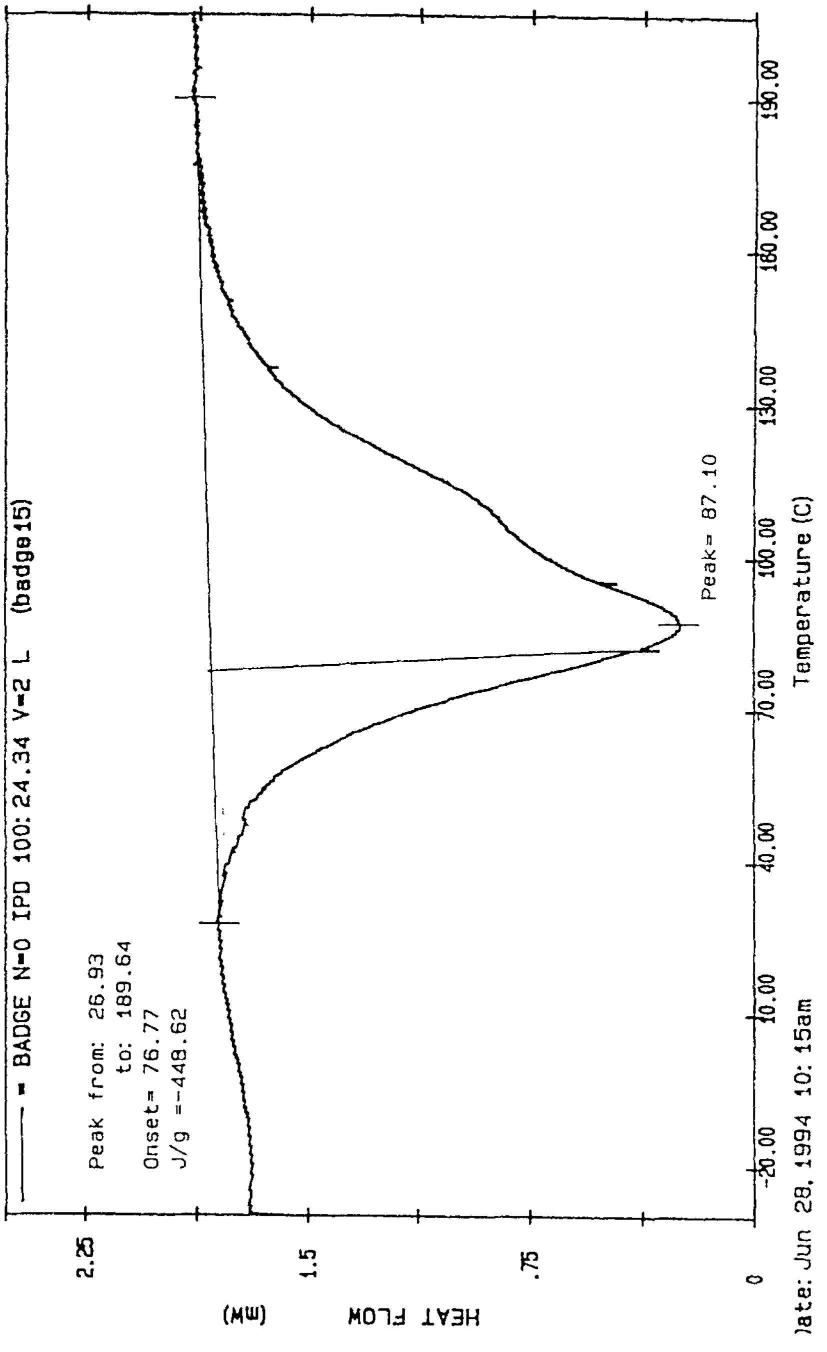

Fig. 2 DSC curve of BADGE ($n=0$)/IPD. Sample mass: 5 mg; Heating rate: 2°C min^{-1}

Results and discussion

Figure 2 shows the dynamic experiment at 2 K min^{-1}, where a peak can be observed at 87.15°C and a shoulder at 111.64°C (peak 1 and peak 2). As previously pointed out, the former corresponds to the reaction between the epoxy resin and the aliphatic group, and the latter to that of the resin with the alicyclic group. This phenomenon was observed in all the experiments carried out at the different scanning rates (Table 1). Figures 3 and 4 show Arrhenius plots for the

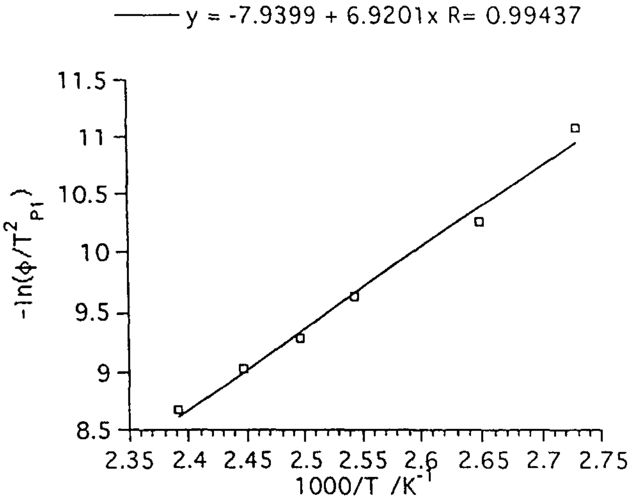

Fig. 3 Arrhenius plot for first peak (T_{p_1})

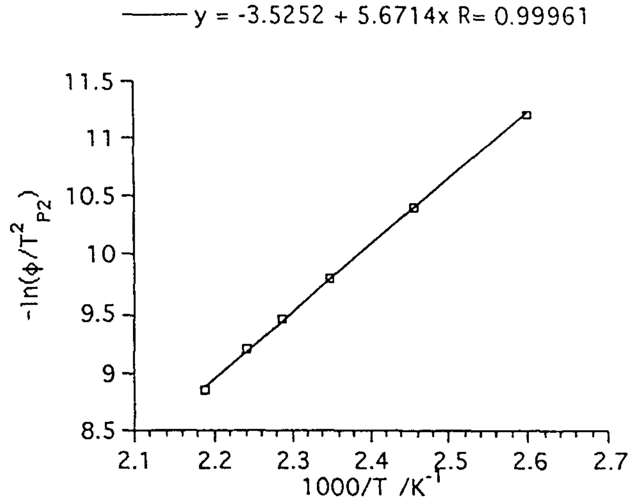

Fig. 4 Arrhenius plot for second peak (T_{p_2})

Table 1 T_{p1} and T_{p2} values corresponding to different heating rates

Φ/K min^{-1}	T_{p1}/K	T_{p2}/K	$1/T_{p1}$	$1/T_{p2}$	$-\ln(\Phi/T^2_{P1})$	$-\ln(\Phi/T^2_{P2})$
2	360.15	384.64	2.73	2.60	11.08	11.21
5	377.48	407.02	2.65	2.46	10.26	10.41
10	392.92	425.76	2.56	2.35	9.65	9.81
15	400.55	437.38	2.50	2.29	9.28	9.46
20	408.45	446.45	2.45	2.24	9.03	9.21
30	418.25	456.85	2.39	2.19	8.67	8.85

two peaks (T_{p_1} and T_{p_2}). From these Figures and by applying Eq. (11), the activation energies and pre-exponential factors and their ratio (k_1/k_2) can be calculated (Table 2).

Table 2 Activation energies and preexponential factors for the two peaks

	E/kJ mol^{-1}	A/s^{-1}
Peak 1	57.48	$3.24 \cdot 10^5$
Peak 2	47.10	$3.21 \cdot 10^3$

The dependences of the constants for peak 1 and 2 on the temperature are obtained directly by using the Arrhenius law. The results are shown in Table 3. Figure 5 illustrates the dependence of k_1/k_2 on temperature.

Table 3 Rate constants k_1 and k_2 and ratio k_1/k_2 at different temperatures

T/K	k_1/s^{-1}	k_2/s^{-1}	k_1/k_2
298.15	$2.70 \cdot 10^{-5}$	$1.76 \cdot 10^{-5}$	1.53
308.15	$5.73 \cdot 10^{-5}$	$3.26 \cdot 10^{-5}$	1.76
318.15	$11.70 \cdot 10^{-5}$	$5.82 \cdot 10^{-5}$	1.99
328.15	$22.70 \cdot 10^{-5}$	$10.02 \cdot 10^{-5}$	2.25
338.15	$41.98 \cdot 10^{-5}$	$16.70 \cdot 10^{-5}$	2.51
348.15	$75.56 \cdot 10^{-5}$	$28.97 \cdot 10^{-5}$	2.80
358.15	$131.72 \cdot 10^{-5}$	$42.60 \cdot 10^{-5}$	3.09
368.15	$222.97 \cdot 10^{-5}$	$65.49 \cdot 10^{-5}$	3.40

The results obtained for the activation energies are in good agreement with those for other epoxy-amine systems [8–10].

Our results show that the activation energies, pre-exponential factors and rate constant k_1/k_2 values are lower for the alicyclic group. It can also be observed that the rate constant ratio increases with increasing temperature. This

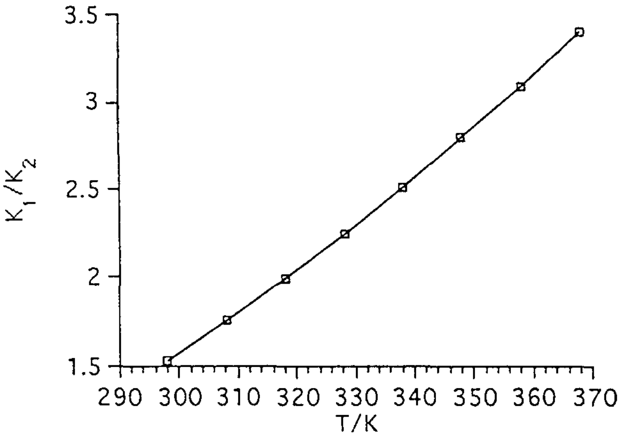

Fig. 5 Rate constant ratio *vs.* temperature

fact must be considered in the choice of an appropriate temperature for a certain reaction. From the fourth column in Table 3, it can be seen that, as the temperature increases, the reaction proceeds mainly through the aliphatic group, while a temperature decrease leads to a higher participation of the alicyclic group in the reaction. These effects can be very interesting when the appropriate reaction temperature is chosen in order to obtain a product with specified properties from an epoxy resin and IPD. In fact, if we need a product with free alicyclic groups, the reaction must take place at a temperature higher than 90°C. On the other hand, if free aliphatic groups are required, the temperature must be below 20°C.

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