Kinetics of epoxy cure: a rapid technique for kinetic parameter estimation

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(Received 14 June 1978; revised 2 October 1978)

A rapid estimation technique is proposed for the determination of the kinetic parameters describing the autocatalytic reaction of epoxy cure. The method utilizes information from a single characteristic point, namely, the point of maximum rate of cure. The proposed method yields results which are in very close agreement with more rigorous regression techniques.

INTRODUCTION

The study of the reaction kinetics of epoxy cure by means of differential scanning calorimetry has been discussed in the literature[1–8]. By assuming that the heat evolved during cure is proportional to the extent of reaction, kinetic parameters have been determined from both isothermal and dynamic experimental data. The epoxy cure reaction has sometimes been described by means of a simple *n*th-order kinetic expression governed by a single rate constant[1–5]. Kinetic expressions describing the autocatalytic behaviour of epoxy cure have also been discussed in the literature[6–8]. These autocatalytic reaction models suggest that the curing process is governed by more than a single rate constant. In all of these studies, the kinetic parameters have been determined by fitting the experimental rate data to the kinetic model using a linear or non-linear least-squares fitting technique, or alternatively, by combining the variables so as to produce a linear relationship from which the kinetic parameters could be estimated.

The present study is concerned with a rapid and accurate estimation procedure for the determination of the kinetic parameters governing the autocatalytic behaviour of epoxy cure. The technique described here is by no means restricted to this particular system, but may be applied successfully to any reaction that can be approximated by the form of kinetic model described in the following section.

Linear and non-linear least-squares regression techniques require detailed information relating to the reaction rate as a function of time at any given temperature. The method described here utilizes only a single characteristic point on the reaction exotherm, namely, the point of maximum rate of heat generation or the peak of the reaction rate curve. For certain forms of the kinetic expression, the values of the peak variables may be suitably combined in order to give an accurate estimate of the kinetic parameters. Even if a more rigorous regression procedure is to be employed, the method described here can provide reliable initial values for the parameter-fitting algorithm. In fact, the success and convergence of many non-linear regression schemes depends critically on the accuracy of the initial estimates.

The method described in the following sections has been successfully tested and applied to a typical liquid epoxy resin cured stoichiometrically with an aromatic diamine.

THEORETICAL ANALYSIS

The curing reaction of epoxy–amine systems can be realistically described by means of the following kinetic expression[7–9]

$$\dot{\alpha} = \frac{d\alpha}{dt} = (K_1 + K_2\alpha^m)(1 - \alpha)^n \qquad (1)$$

where $\dot{\alpha}$ is the rate of reaction, α is the degree of cure, K_1 and K_2 are the kinetic rate constants, and m and n are kinetic exponents. Equation (1) can be readily rearranged to the following form

$$m = \frac{\ln\left(\dfrac{\left(\dfrac{\dot{\alpha}}{(1-\alpha)^n} - K_1\right)}{K_2}\right)}{\ln\alpha} \qquad (2)$$

Initially when $t = 0, \alpha = 0$ and equation (1) reduces to

$$\left(\frac{d\alpha}{dt}\right)_{t=0} = K_1 \qquad (3)$$

Equation (3) indicates that the kinetic rate constant K_1 is readily determined directly from isothermal reaction rate data. The maximum or peak of the reaction rate curve is defined by

$$\frac{d^2\alpha}{dt^2} = 0 \qquad (4)$$

Applying this condition to the kinetic expression given by equation (1) yields

$$nK_1\alpha_P^{1-m} + K_2(m+n)\alpha_P - mK_2 = 0 \qquad (5)$$

where the subscript P has been used to denote the value at the peak. The reaction kinetics for this epoxy–amine system have been found to be accurately described by means of a second-order kinetic expression, irrespective of

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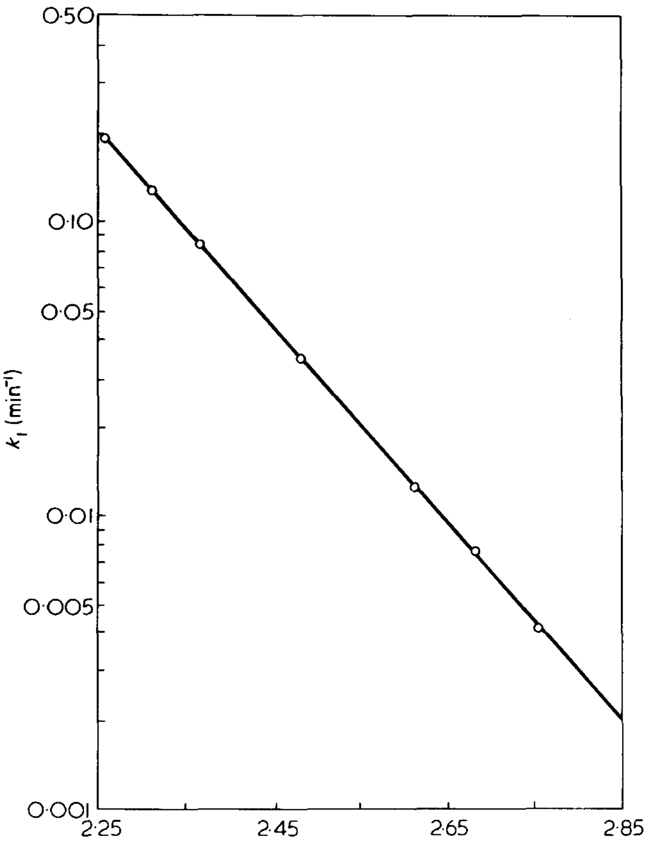

Figure 1 Kinetic rate constant, K_1, as a function of reciprocal absolute temperature

temperature[7–9]. Therefore, assuming that the overall reaction order for the epoxy–amine system is of second order yields

$$m + n = 2 \tag{6}$$

and equation (5) reduces to

$$K_2 = \frac{(2 - m)K_1\alpha_P^{1-m}}{m - 2\alpha_P} \tag{7}$$

Expressing equation (2) at the peak and substituting equation (7) yields

$$m = \frac{\ln\left(\dfrac{\left(\dfrac{\dot{\alpha}_P}{(1-\alpha_P)^{2-m}} - K_1\right)}{\left(\dfrac{(2-m)K_1\alpha_P^{1-m}}{m - 2\alpha_P}\right)}\right)}{\ln\alpha_P} \tag{8}$$

Equation (8) is an implicit expression in the parameter m. The quantities K_1, $\dot{\alpha}_P$, and α_P are readily determined at any given temperature using differential scanning calorimetry. These experimentally determined values may then be substituted in equation (8) which is solved numerically in order to determine the parameter m. The kinetic rate constant K_2 is then determined from equation (7).

EXPERIMENTAL

Materials

The experimental studies were conducted with a commercial diglycidyl ether of bisphenol-A (Allied Resin Corporation, DER-332). The liquid epoxy resin was cured with a stoichiometric amount of *m*-phenylene diamine (Aldrich Chemical Co., purissimum grade 99+%). These materials were used as supplied without any further purification. The epoxide equivalent weight of the resin and of the amine were taken as 174 and 27 respectively.

Equipment and procedure

Experimental measurements were carried out using a Perkin–Elmer differential scanning calorimeter (Model DSC-1B). This instrument was calibrated within the required temperature range from the known melting points of high purity elements (d.s.c. calibration standards) and organic compounds (Fisher thermetric standards).

Isothermal experiments were conducted in the temperature range 343–443K in order to obtain both the cure rate and extent of cure as a function of time. The isothermal baseline was established at the pre-selected cure temperature and range setting by using a fully-cured sample and an empty sample pan. Samples were prepared by mixing appropriate amounts of epoxy and amine. A 10–20 mg portion was sealed in a volatile sample pan and introduced into the sample holder. Observed weight losses were negligible in all cases. The exothermic reaction was considered to be complete when the recorder pen levelled off to the initial isothermal baseline. Further details relating to the experimental procedure are described elsewhere[9].

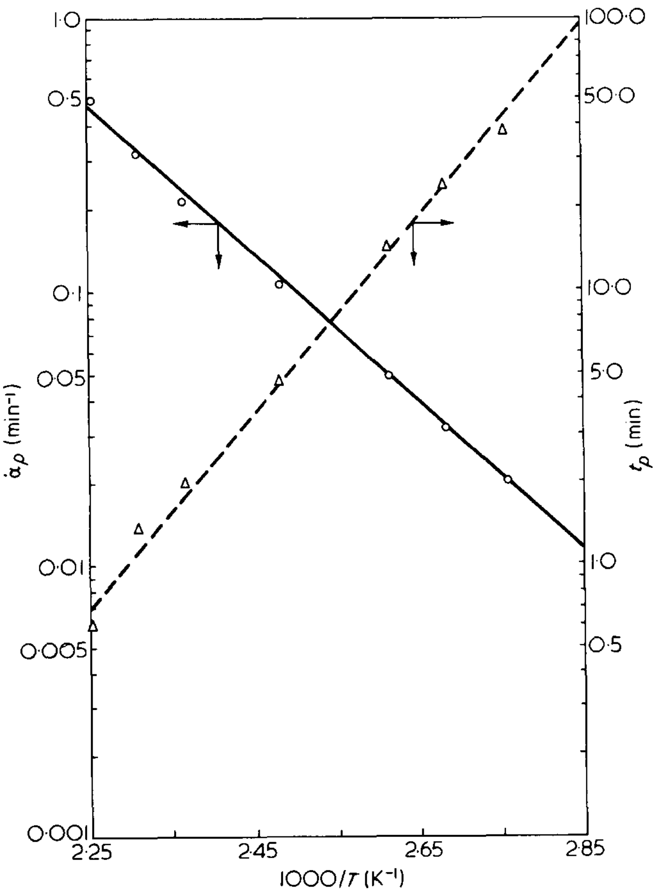

Figure 2 $\dot{\alpha}_p$ and t_p as a function of reciprocal absolute temperature

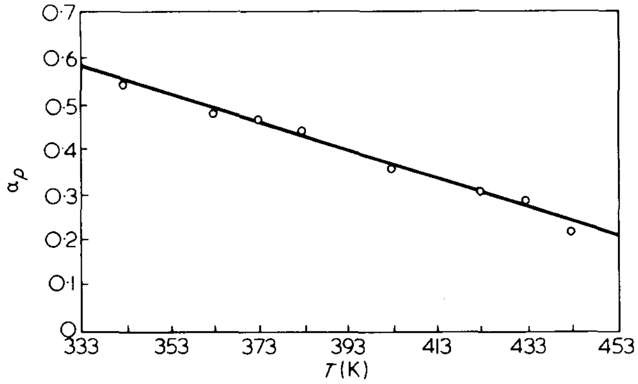

Figure 3 Variation of α_p with temperature

Table 1 Temperature dependence of kinetic variables

Kinetic variable	Temperature dependence	Correlation coefficient
K_1 (min^{-1})	$7.67 \times 10^6 \exp\left(\frac{-6.45 \times 10^7 *}{RT}\right)$	–0.996
$\dot{\alpha}p$(min^{-1})	$3.72 \times 10^5 \exp\left(\frac{-5.04 \times 10^7}{RT}\right)$	–0.998
t_p (min)	$6.62 \times 10^{-9} \exp\left(\frac{6.82 \times 10^7 *}{RT}\right)$	0.994
αp	$1.61 - 3.07 \times 10^{-3}\, T$	–0.991

* J/kgmol

The cumulative heat generated during cure was obtained as a function of time by numerically integrating the rate data using Simpson's one-third rule with the aid of a digital computer (Cyber CDC 173). Alternatively, cumulative heat generation could be obtained by integrating the rate signal directly through the use of an analog computer[7,8].

RESULTS AND DISCUSSION

The kinetic rate constant, K_1, which is the initial reaction rate at a given temperature, was determined directly from the reaction rate curve. As can be seen in *Figure 1*, K_1 was found to follow an Arrhenius dependence on temperature. The corresponding activation energy was found to be 6.44 x 10^7 J/kgmol (15.4 kcal/gmol). The maximum isothermal reaction rate, $\dot{\alpha}_P$, the degree of cure at this maximum rate, α_P, and the reaction time required to attain this maximum rate, t_P, were also found to be functions of temperature. The temperature dependence of both $\dot{\alpha}_P$ and t_P is presented in *Figure 2*. An increase in temperature increases the maximum reaction rate, $\dot{\alpha}_P$, but decreases the time required to reach the peak, t_P. As is evident from *Figure 2*, the temperature variation of both $\dot{\alpha}_P$ and t_P can be accurately described by means of an Arrhenius relationship. The conversion at the maximum reaction rate, α_P, was observed to follow a linear variation with temperature as shown in *Figure 3*. The temperature dependence of K_1, $\dot{\alpha}_P$, t_P and α_P is summarised in *Table 1*.

These experimental results were used in order to test the validity and applicability of the method described by equations (7) and (8). For a given cure temperature, T, the experimentally measured values for K_1, $\dot{\alpha}_P$, and α_P were used in equation (8) in order to determine the kinetic parameter m. Equation (8) was solved numerically by means of a Newton–Raphson technique. A comparison between the values of m as determined by means of equation (8) and the values of m obtained by means of a non-linear least-squares fit[10] of equation (1) to the experimental rate data, is shown in *Figure 4*. Reasonably good agreement is obtained between these two methods.

The calculated values of m from equation (8) were then substituted into equation (7) in order to determine the kinetic rate constant K_2. A comparison between the values of K_2 obtained by this means and the values obtained by fitting the kinetic model described by equation (1), is shown in *Figure 5*. Very close agreement was obtained in

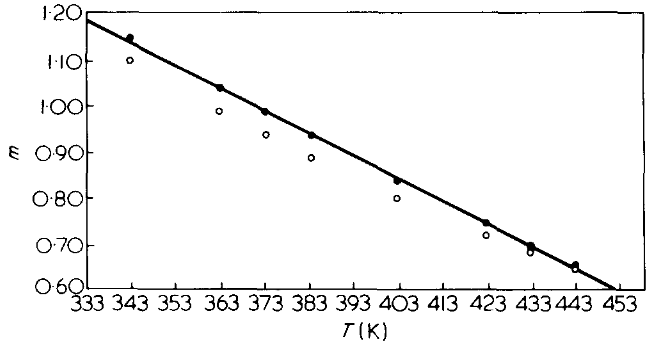

Figure 4 Variation of kinetic parameter m with temperature ●, Equation (8)

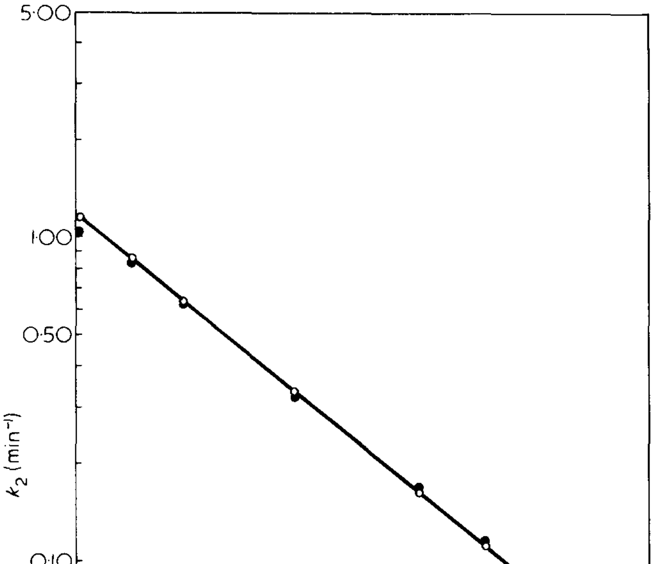

Figure 5 Kinetic rate constant, K_2, as a function of reciprocal absolute temperature. ●, Equation (7)

all cases. The kinetic rate constant K_2 can be seen to follow an Arrhenius dependence on temperature having an activation energy of 4.56×10^7 J/kgmol (10.9 kcal/gmol). Similar values for the activation energy of epoxy–amine systems have been reported in the literature[1–8].

CONCLUSIONS

The kinetic parameters describing epoxy cure are readily estimated from the initial reaction rate and information available at the peak of the reaction rate curve. The results obtained using this method were found to be in close agreement with the values obtained by fitting the kinetic model to the experimental reaction rate data. Prior knowledge regarding the overall reaction order of the system is necessary for the method to be applicable.

ACKNOWLEDGEMENTS

The authors would like to express their gratitude to Allied Resin Corporation for supplying the liquid epoxy resin and to the State University of New York for financial support.

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