

Cure Mechanism of a Modified Nitrile Epoxy Adhesive

By using an adhesive for structure bonding of metal-to-metal honeycomb sandwich, structural plastic laminates and fiber-reinforced composites is gaining in popularity as a fastening method in all spheres of engineering and industry. Since bonding can be carried out at relatively lower temperatures than the traditional welding techniques, and no holes are needed as in riveted and bolted joints, a more uniform stress takes place when the chemically bonded laminates are loaded. However, experience has told us that the mechanical properties and performance of adhesive bonds are strongly dependent on the curing conditions.¹ Higher temperatures or longer curing times may result in brittle adhesive layers and reduce the impact strength. On the other hand, the curing reaction may not be fully complete, and the mechanical properties may change during use if the temperature is too low. Therefore, an understanding of the curing mechanism of an adhesive is essential to control and optimize mechanical properties and performance of a structure-bonded laminate.

A variety of experimental techniques has been developed to study the kinetics of thermosetting reactions.²⁻⁹ One is to use the differential scanning calorimeter to measure the heat generated during the cure. This method has been employed by a number of workers to investigate the cure mechanism of epoxy, polyester, and phenolic resins.⁷⁻¹⁶ Prime expressed the reaction kinetics by a simple n th-order equation.^{7,8} Kamal and co-workers proposed a very realistic model to describe the dependence of the rate of cure on time and temperature.⁹⁻¹² Their empirical expression consists of two reaction-rate constants and two reaction-order parameters. This model has been proven satisfactorily for describing the experimental data for a liquid epoxy resin and for injection-molding grade epoxy, phenolic, and polyester resins.⁹⁻¹⁵ However, in all these studies, the kinetic parameters were determined by means of data fitting using a complicated nonlinear, least-square method. In order to overcome this deficiency, Ryan and Dutta recently proposed a rapid estimation technique for the determination of these parameters.¹⁶ However, the total reaction order for curing was assumed to be a constant in their analysis.

In this short note, we attempt to explore the feasibility of using Kamal's model to determine the curing kinetics of a modified nitrile epoxy adhesive. In addition, as an extension of Ryan and Dutta's work, a quick and simple estimation procedure is proposed to determine the kinetic parameters, if the empirical mathematical equation for reaction has one reaction-rate constant and two reaction-order parameters.

KINETIC MODEL

If the curing reaction obeys the following expression,

$$\frac{d\alpha}{dt} = k\alpha^m(1-\alpha)^n \quad (1)$$

where α is the degree of reaction or cure, $d\alpha/dt$ is the reaction rate, k is the reaction rate constant, and m and n are the reaction orders, the relationship between m and n may be readily related if there is a maximum in the isothermal reaction-rate and time curve. In other words, because $d^2\alpha/dt^2 = 0$ at the maximum, we obtain

$$\frac{m}{m+n} = \alpha_p \quad (2)$$

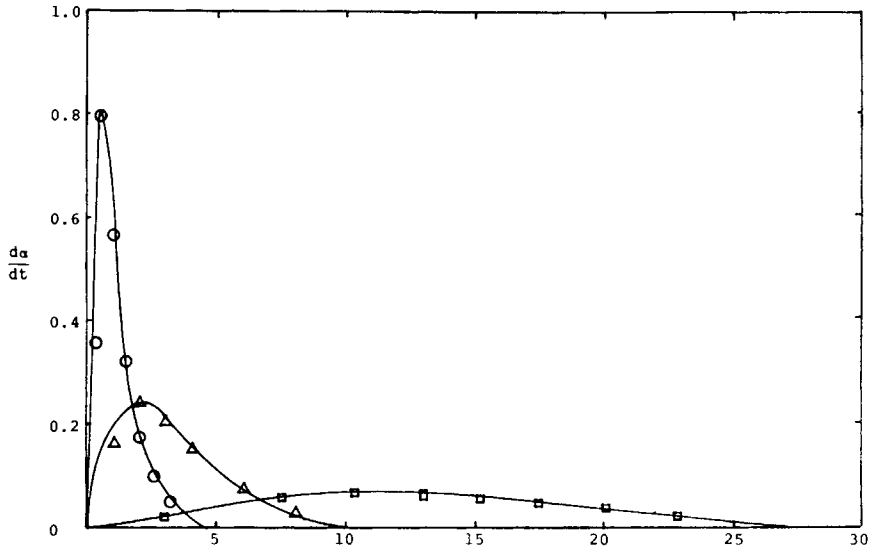


Fig. 1. Isothermal reaction rate as a function of time: (○) 423 K; (△) 403 K; (□) 383 K; (—) calculated.

where α_p denotes the value of α at the peak. Since α_p changes with the cure temperature, eq. (2) implies that both m and n may vary with temperature; however, the ratio of reaction order, $m/(m+n)$, and α_p have the same dependence on temperatures. Substituting eq. (2) into eq. (1) yields the following equation to determine the reaction rate constant k and reaction order m :

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln k + m \left[\ln \alpha + \left(\frac{1-\alpha_p}{\alpha_p}\right) \ln(1-\alpha) \right] \quad (3)$$

EXPERIMENTAL

A modified nitrile epoxy adhesive purchased from American Cyanamid Co. was used in this study. This polymeric film has been widely used for structure bonding of epoxy-carbon fiber

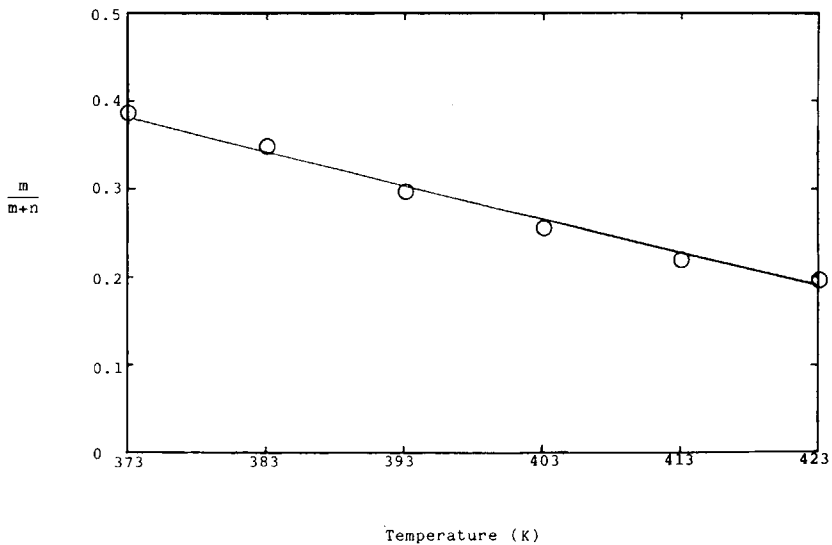
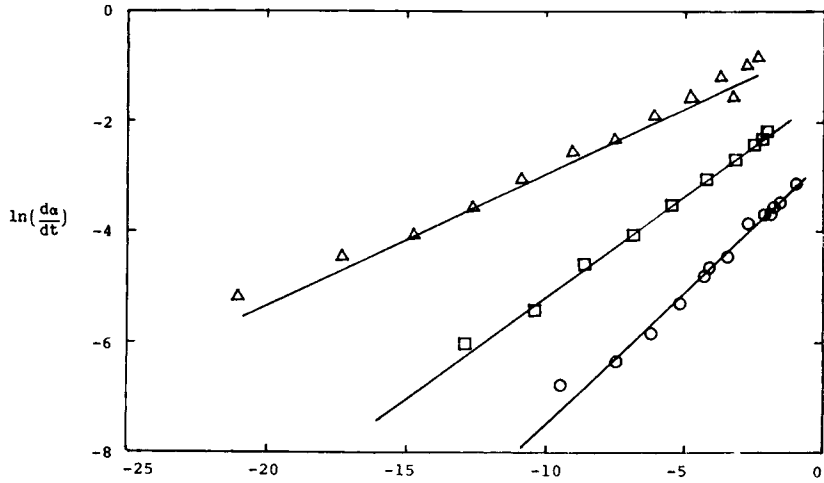


Fig. 2. Temperature dependence of the ratio of kinetic orders.



$$\left[\ln \alpha + \left(\frac{1-\alpha p}{a_p} \right) \ln (1-\alpha) \right]$$

Fig. 3. Variation of parameters m and k with temperature (K): (Δ) 413; (\square) 393; (\circ) 373.

composite laminates. A Perkin-Elmer differential scanning calorimeter (Model DSC II) was employed to measure the heat evolved as a function of time during the isothermal curing runs. Experiments were conducted in the temperature range of 373–423 K. The reaction was assumed to be complete at a given temperature when the recorder pen levelled off to the baseline. The sample was reweighed after the reaction was complete, and the observed weight loss was found to be negligible.

RESULTS AND DISCUSSION

Figure 1 shows the experimental results for the rate of reaction as a function of time at different temperatures. Integrating the reaction rate with respect to time gives the degree of

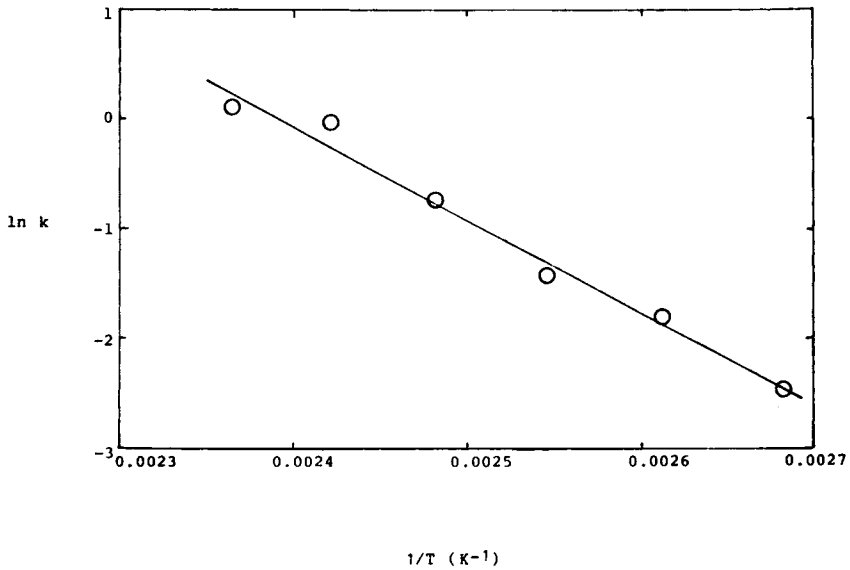


Fig. 4. Logarithm of k as a function of reciprocal absolute temperature.

reaction or cure variation with time. The ratio of reaction order, $m/(m + n)$, may therefore be determined using the procedure suggested by eq. (2), and its relationship with temperature is illustrated in Figure 2 and can be expressed as follows:

$$\frac{m}{m+n} = 1.8415 - 0.003914T$$

The negative slope in this figure implies that ratio of m to n decreases as the curing temperatures increases. A similar result has been reported in the literature for epoxy and phenolic materials.¹⁴⁻¹⁶

In order to determine m and k and to test the validity and applicability of the method described by eqs. (2) and (3), experimental data were fitted into eq. (3). As is evident from Figure 3, the agreement is very satisfactory. Therefore, parameters m and k can be readily determined by means of a linear least-squares method. The best data fit for m is

$$m = 3.156 - 0.00704T$$

The dependence of rate constant, k , on temperature is plotted in Figure 4, and shows the relationship obeys an Arrhenius expression. The corresponding activation energy was found to be 16.91 kcal/mol. This value is slightly higher than that of epoxyamine systems (14–16 kcal/mol) reported in the literature.^{9,15,16} This difference may be due to the effect of nitrile on the cure mechanism of the epoxy-dominated adhesive.

Finally, a comparison between the experimental results and the theoretical prediction calculated using the current method and data is also shown in Figure 1. The agreement is satisfactory. It can be concluded from this analysis that the present model is valid, and gives a much simpler approach to determining the kinetic parameters of thermosetting polymers.

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