

# Autocatalytic Cure Kinetics from DSC Measurements: Zero Initial Cure Rate\*

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## Synopsis

A new, simplified technique for obtaining the kinetic parameters of an autocatalyzed cure reaction from isothermal DSC measurements is presented. The method is appropriate to reactions that have a zero initial rate and relies solely upon characteristics of the exotherm peak with no assumptions being made about the overall reaction order. This technique is illustrated by obtaining the phenomenological cure kinetics of a commercial epoxy film adhesive. The derived kinetic model reproduces the measured isotherms in their entirety. In addition, the predictive capability of the model is demonstrated by comparison with an independent measurement of the adhesive's low temperature curing behavior. Glass transition temperature measurements are also made on partially cured samples and a good correlation with the degree of cure is found.

## INTRODUCTION

Knowledge of the rate that an adhesive cures and how that rate varies with cure temperature is useful and important from several standpoints. Foremost among these is to ensure that the adhesive is processed in a manner compatible with its end use. In addition, the rate of cure defines the shelf life of the adhesive for a given set of storage conditions and its working life by controlling its tack, wetting, and flow properties. For a commercial adhesive, the manufacturer's recommended cure schedule will, in general, yield an adequately cured material. It is often desired, however, to cure the adhesive under a different set of conditions. This will occur, for instance, when several materials in an assembly are to be simultaneously cured or if temperature sensitive components are to be bonded. The cure kinetics in the form of a phenomenological rate law permit the cure cycle to be optimized for a given bonding situation. If, in addition, correlations between the degree of cure and the cohesive strength of the adhesive have been established, they help to make certain that the adhesive joint has not been compromised by cure cycle changes.

In general terms, the cure kinetics can be described by a rate law given by

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

where  $\alpha$  is the extent of cure,  $k$  is the Arrhenius rate constant, and  $f(\alpha)$  is a function that depends on the reaction mechanism. A commercial epoxy

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adhesive formulation is a complex mixture of resins, hardeners, modifiers, accelerators, and fillers. As such, there is little hope that insight into the nature of  $f(\alpha)$  can be obtained without detailed and extensive chemical analysis.<sup>1,2</sup> Nevertheless, chemical kinetic information is required for process definition, and it will be shown that  $f(\alpha)$  can be treated in a phenomenological manner to rapidly and inexpensively obtain a useful kinetic model without requiring a thorough understanding of the cure chemistry. In the present investigation, a rapid method for estimating cure kinetics from isothermal differential scanning calorimetry (DSC) measurements during cure is presented. The method is appropriate to a variety of materials that exhibit autocatalytic cure behavior and whose initial cure rate is zero. The technique is illustrated by deriving a rate law for the cure of a commercial epoxy film adhesive. The resulting rate law is shown to describe as well as predict the extent of cure during an isothermal cure.

### EXPERIMENTAL

A commercial film adhesive, FM123-5, was used in this study. FM123-5, obtained from the American Cyanamid Co., is a nitrile modified-dicyandiamide (DICY) cured epoxy adhesive that is supported on a nylon carrier. The adhesive was stored in a freezer and under desiccation prior to use. Samples consisting of  $\approx 15$  mg of adhesive were placed in aluminum DSC pans and were run on a Perkin-Elmer DSC-2. The DSC-2 is interfaced to an LSI 11/23 microcomputer to facilitate data acquisition and analysis and was calibrated for temperature and enthalpy with thermal standards. Isothermal cures were carried out at six temperatures between 100 and 140°C. The DSC measurements were terminated when the signal returned to the baseline. Subsequent to the isothermal cures, the samples were scanned at 10°C/min to verify that the cures were complete. The 100 and 110°C samples showed residual curing exotherms that corresponded to  $0.036\Delta H_R$  (heat of reaction) and  $0.014\Delta H_R$ , respectively.  $\Delta H_R$ , in this case, was computed by adding the residual exotherm to the integrated heat from the isothermal run. Glass transition temperatures  $T_g$  were determined for partially cured adhesive by DSC at a heating rate of 10°C/min and were taken as the extrapolated onset of the transition region.

### METHOD OF KINETIC ANALYSIS

The relationship between an isothermal DSC signal and the rate and extent of cure has been reviewed recently.<sup>3</sup> A general rate law that has proven useful for studying the epoxy cure reaction is<sup>4-7</sup>

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

This rate law, which describes an autocatalytic reaction, embodies the experimental observations that the peak in the exotherm occurs at some  $t > 0$  and that the rate of reaction at  $t = 0$  may be nonzero. In the case of FM123-5,

$(d\alpha/dt) (t = 0)$  is sensibly zero for all temperatures; thus  $k_1 = 0$  and

$$\frac{d\alpha}{dt} = k\alpha^m(1 - \alpha)^n \tag{3}$$

The kinetic parameters can be obtained by fitting the isothermal data with nonlinear least squares procedures or from simplified techniques that depend on characteristics of the exotherm. Ryan and Dutta<sup>8</sup> have proposed a method for estimating the parameters in eq. (2) that depends on the extent of reaction at the exotherm peak  $\alpha_P$  as well as the rate of reaction at the peak  $\dot{\alpha}_P = (d\alpha/dt) (t = t_P)$ . The method suffers, however, from requiring prior knowledge of the overall reaction order  $(m + n)$ . A recent extension of this technique<sup>9</sup> that applies to eq. (3) and makes no assumptions concerning the reaction order involves relating  $m$  and  $n$  by  $\alpha_P = m/(m + n)$  and fitting the linear equation

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln k + m \left[ \ln \alpha + \left(\frac{1 - \alpha_P}{\alpha_P}\right) \ln(1 - \alpha) \right] \tag{4}$$

Unfortunately, this method still requires least squares fitting where careful attention must be paid to proper weighting of the data. Misleading results may also be obtained if degradation or diffusion control occurs at long times.

In this paper, an extension to Ryan and Dutta's method that requires neither data fitting nor prior knowledge of the reaction order is proposed. The three kinetic parameters in eq. (3),  $k$ ,  $m$ , and  $n$ , can be determined from the three characteristics of the exotherm peak, namely,  $\alpha_P$ ,  $\dot{\alpha}_P$ , and  $t_P$ , where  $t_P$  is the location of the peak in time. It is easily shown that

$$\alpha_P = \frac{m}{(m + n)} \tag{5}$$

$$\dot{\alpha}_P = k \frac{m^m n^n}{(m + n)^{(m+n)}} \tag{6}$$

and

$$t_P = \frac{1}{k} \int_0^{\alpha_P} \frac{d\alpha}{\alpha^m(1 - \alpha)^n} \tag{7}$$

where use has been made of the fact that  $(d/dt) (d\alpha/dt) = 0$  at the peak. Multiplying eqs. (6) and (7) together and rearranging yields

$$n = \left[ \frac{\dot{\alpha}_P t_P (m + n)^{(m+n)}}{m^m \int_0^{\alpha_P} \frac{d\alpha}{\alpha^m(1 - \alpha)^n}} \right]^{1/n} \tag{8}$$

where  $m$  is given by  $m = n\alpha_P/(1 - \alpha_P)$ . Equation (8) can be numerically solved for  $n$ , and  $m$  and  $k$  follow from eqs. (5) and (6), respectively.

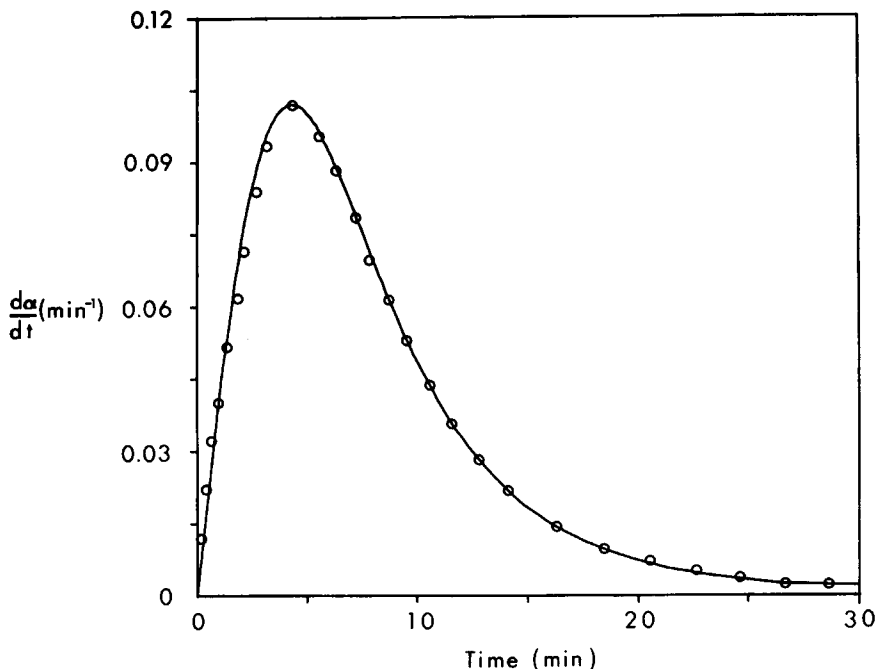


Fig. 1. Rate of cure of FM123-5 as a function of time at 120°C. The symbols represent the measured isotherm and the smooth curve is from the derived rate expression.

### ISOTHERMAL DSC RESULTS

Isothermal cure measurements on FM123-5 were made at 100, 110, 115, 120, 130, and 140°C and analyzed as described above. Figure 1 displays the observed rate of cure as a function of time at 120°C (symbols) along with the curve predicted by eq. (3) and the kinetic parameters. The corresponding  $\alpha$  vs.  $t$  relationship is shown in Figure 2. The excellent agreement, which is typical, validates the kinetic model and the analysis procedure. The rate constants exhibit Arrhenius behavior, as shown in Figure 3, and are given by

$$\log k = 12.290(5) - 5040(62)/T \quad (9)$$

The activation energy of 23.1(3) kcal/mol agrees with literature values for other epoxy resins cured with DICY.<sup>10,11</sup> The exponents in the rate law are found to vary with cure temperature as evidenced by  $\alpha_p$  varying in a regular manner with the cure temperature. This behavior has been observed in a similar adhesive<sup>9</sup> as well as other curing systems.<sup>8,12,13</sup> The variation of  $\alpha_p = m/(m+n)$  with cure temperature is shown in Figure 4. The relationship is described by the straight line

$$m/(m+n) = 1.1778(12) - 0.002256(95)T \quad (10)$$

with a correlation coefficient of  $-0.996$ . Figure 5 displays the variation of  $m$  with  $T$ .  $m$  exhibits a minimum near 120°C with a sharp increase for larger temperatures and a more gradual rise at smaller temperatures. The tempera-

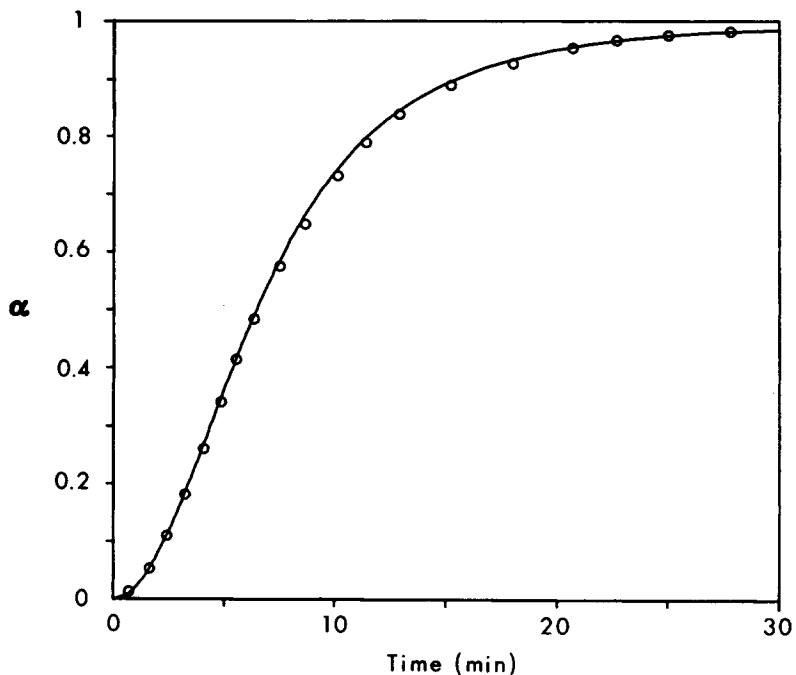


Fig. 2. Degree of cure with time at 120°C. The curve is from the rate law, and the symbols are the measured values.

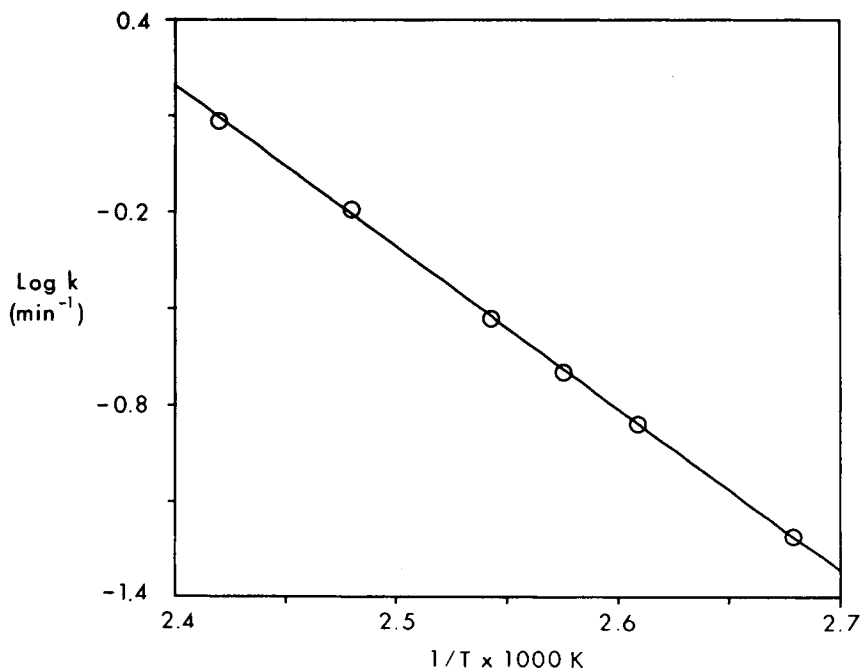


Fig. 3. Arrhenius plot of the temperature dependence of the rate constants for FM123-5. The activation energy is 23.1(3) kcal/mol.

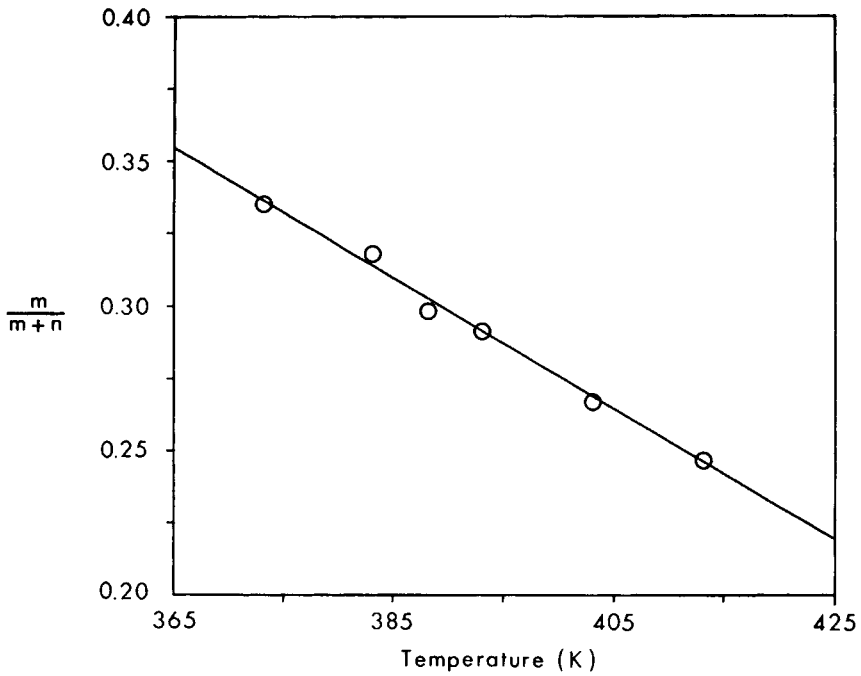


Fig. 4. Temperature dependence of  $\alpha_p = m/(m+n)$ .

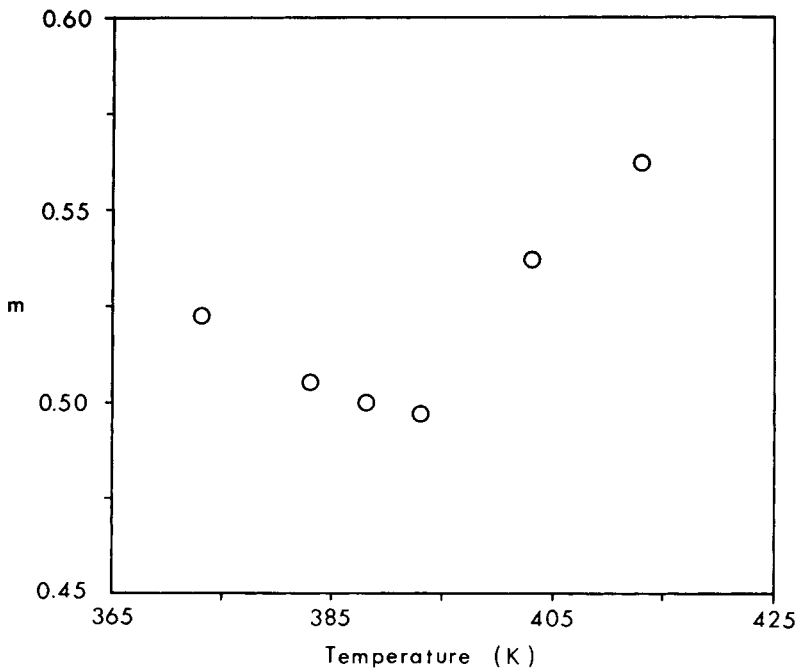


Fig. 5. Temperature dependence of the exponent  $m$  in the rate law.

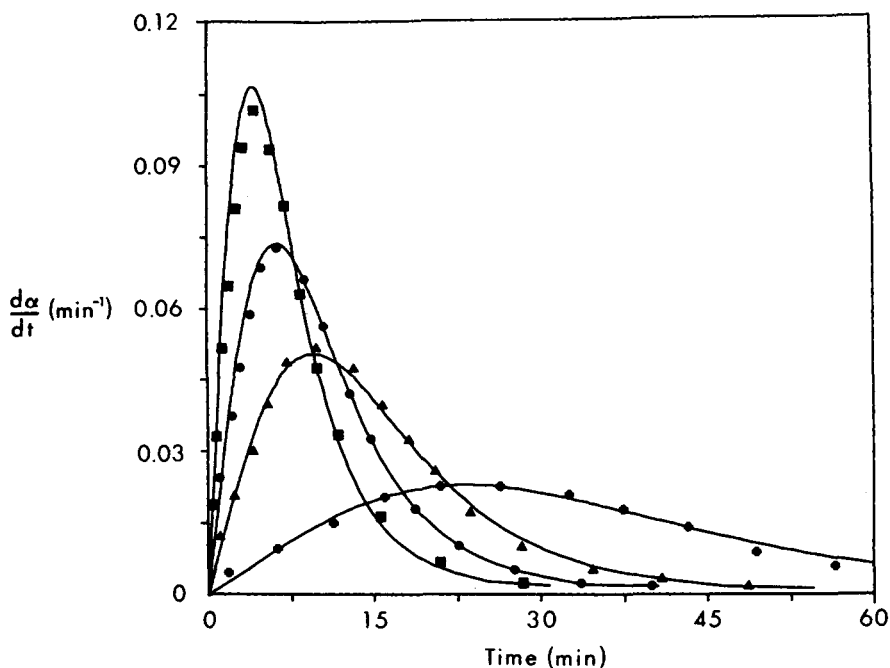


Fig. 6. Comparison of the measured cure rates at 100 (+), 110 (▲), 115 (●), and 120 (■) °C with the predictions of the kinetic model.

ture variation of the exponents indicates that the reaction mechanism changes with temperature. This is to be expected since DICY/epoxy systems undergo a complex series of curing reactions,<sup>14,15</sup> some of which only occur at relatively high temperatures or once the DICY is exhausted. It should be emphasized that the derived rate law, in this case, is strictly phenomenological. It is used solely for descriptive purposes, and no fundamental significance is attached to the kinetic parameters.

From a practical standpoint, we are primarily concerned with the low temperature ( $T < 100^{\circ}\text{C}$ ) curing behavior of FM123-5. In order to put the kinetic model into a form that is suitable for predicting the cure rate at these temperatures,  $m$  will be described by a straight line through the four lowest temperatures:

$$m = 1.0083(14) - 0.00131(19)T \quad (11)$$

While  $m$  does not appear to be strictly linear over this region; it is changing slowly enough that significant error should not be encountered over narrow temperature ranges. The measured isothermal curves for 100, 110, 115, and 120°C are compared, in Figure 6, with those predicted by eqs. (3), (9), (10), and (11). Once again, agreement is very good.

#### LOW TEMPERATURE CURING OF FM123-5

The most stringent test of a kinetic scheme is its ability to predict reaction rates at temperatures outside of the range of determination and for different

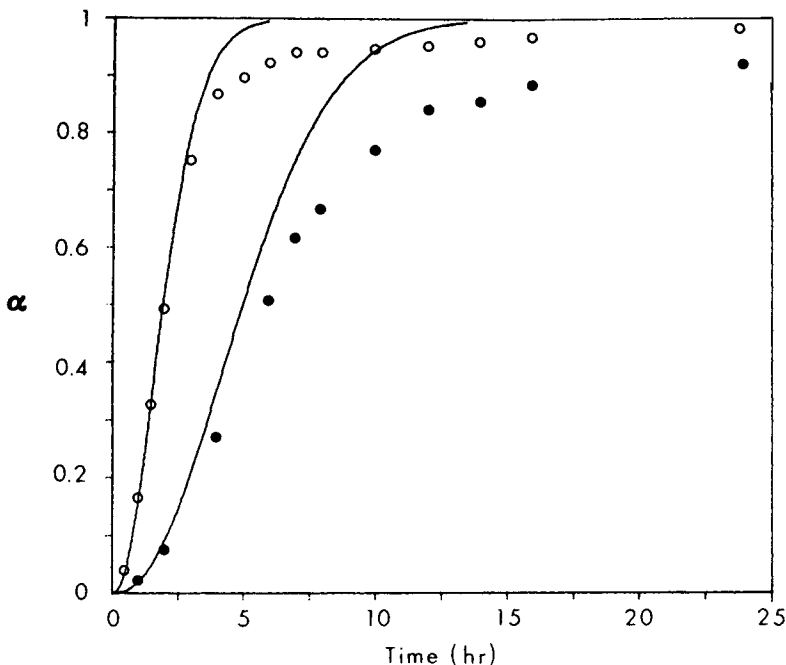


Fig. 7. Degree of cure as a function of cure time at 75 (●) and 85 (○) °C. The kinetic model predictions are shown by the curves.

measurement techniques. This was accomplished, in the case of FM123-5, by curing the adhesive, in DSC pans, in an oven at 75 or 85°C for varying periods of time. The small samples were placed on a large aluminum block to ensure immediate temperature equilibrium. After removal from the oven, the adhesive was scanned in the DSC at a heating rate of 10°C/min to determine the residual heat of curing  $\Delta H$ . The degree of cure is then calculated from

$$\alpha(t, T) = 1 - \frac{\Delta H}{\Delta H_R} \quad (12)$$

Figure 7 shows  $\alpha$  at 75 and 85°C as a function of cure time along with the kinetic model predictions. The agreement is very good at small times, whereas, at long times, the adhesive vitrifies and the curing reaction becomes diffusion limited. At that point, the reaction is effectively quenched, and the end product is an undercured adhesive. The kinetic model is still useful, however, for predicting the time required to attain the ultimate state of cure at a given cure temperature. In general, the results demonstrate the utility of the kinetic model.

An added advantage of measuring  $\alpha$  by dynamic DSC is that the glass transition temperatures  $T_g$  of the partially cured samples can be obtained from the same thermograms.  $T_g$  as a function of  $\alpha$  for the partial cures at 75 and 85°C are shown in Figure 8. The correlation is very good and is independent of cure temperature. The data can be represented by two straight line segments that intersect at  $\alpha \approx 0.8$ . At small degrees of cure, the increase in  $T_g$



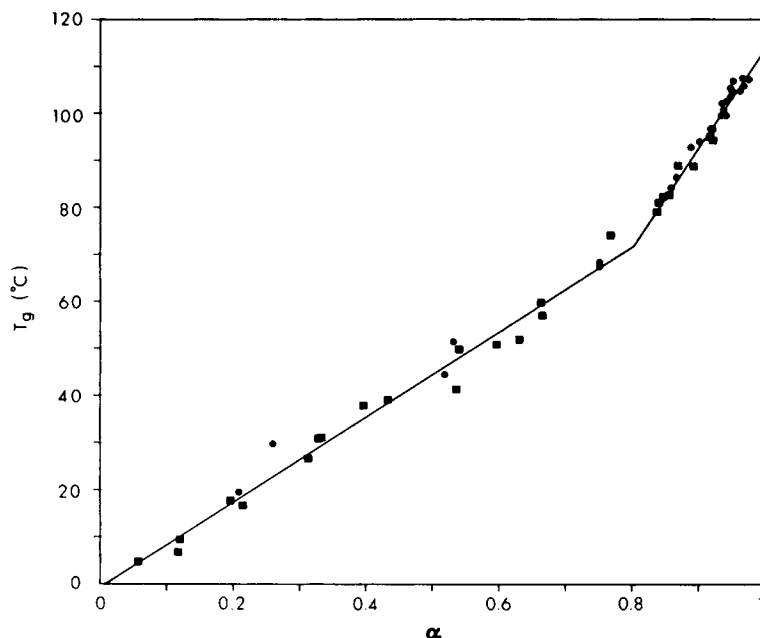


Fig. 8. Glass transition temperatures for FM123-5 partially cured at 75 (■) and 85 (●) °C.

is due to increasing molecular weight of the epoxy resin, whereas, at high conversion, an increasing  $T_g$  results from higher crosslink densities.<sup>16,17</sup> Similar behavior has been observed before, and, in one case, mechanical testing indicated that the intersection of the two lines occurred at the gel point.<sup>18</sup> The correlation between  $\alpha$  and  $T_g$  permits  $T_g$  to be used as a diagnostic for the degree of cure provided that the temperature history of the sample is known (i.e., no degradation has occurred) and factors such as the moisture content of the adhesive are accounted for.

### CONCLUSION

A simple, rapid method for kinetic parameter estimation from isothermal DSC measurements has been proposed. The technique is appropriate to autocatalyzed reactions and was applied to the cure of a commercial epoxy film adhesive. The kinetic model described the measured isothermal DSC curves and adequately predicted the rate of cure at two temperatures below the temperature range of the kinetic determination. In addition, a good correlation was found between  $T_g$  and the degree of cure. This indicates that a kinetic model, in conjunction with  $T_g$  measurements, can be used for diagnostic as well as for quality control purposes in a production environment.

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