Determination of autocatalytic kinetic model parameters describing thermoset cure

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INTRODUCTION

The kinetic behavior of thermoset matrices for high-performance composites has been widely reported as an important phenomenon driving the morphological changes of the polymer structure during processing operations. In fact, the combination of the kinetic model of the resin cure reaction with heat transfer and chemorheological models has been used[1-7] as a basis of general models describing the temperature, degree of polymerization, and viscosity of the matrix as a function of processing conditions, tool characteristics, and material properties, in different composite technologies (autoclave lamination, pultrusion, resin transfer molding, filament winding, etc.).

Cure kinetic models are generally developed by analyzing experimental results obtained by different thermal analysis techniques. Excellent reviews on this topic are available.[8,9] In particular, differential scanning calorimetry (DSC) has been widely used, assuming a proportionality between the heat evolved during the cure [$H(t)$] and the extent of reaction (α) through the following equations:

$$\alpha = H(t)/H_{ult} \qquad (1)$$

$$d\alpha/dt = (1/H_{ult})dH/dt \qquad (2)$$

where H_{ult} is the total heat developed in the process at full conversion. Although several simultaneous reactions are occurring during the polymerization process, simple models based on the assumption that only one reaction can represent the whole cure process have been developed for modeling purposes.[8-14] The most simple model corresponds to an nth-order kinetic expression[8,9]:

$$d\alpha/dt = k(1 - \alpha)^n \qquad (3)$$

where n is the reaction order, and k, the rate constant given by an Arrhenius temperature dependence:

$$k = k_0\exp(-E/RT) \qquad (4)$$

k_0 is the preexponential constant; E, the activation energy; and T, the absolute temperature. For an isothermal test,

eq. (3) predicts a maximum of the reaction rate at time $= 0$. Then, if an isothermal process is characterized by a thermogram showing a maximum of the reaction rate at some point other than the reaction start, the kinetic model given by eq. (3) cannot be applied and the so-called autocatalytic model, with two kinetic constants (k_1, k_2) and two reaction orders (**m, n**), must be used:

$$d\alpha/dt = (k_1 + k_2\alpha^m)(1 - \alpha)^n \qquad (5)$$

Furthermore, eq. (5) also predicts the kinetic behavior of some thermosets characterized by a zero initial reaction rate ($k_1 = 0$).[5]

The model represented by eq. (5) has been successfully applied to autocatalytic polymerization reactions where one of the products of the cure process acts as a catalyst of the same reaction as in the cure of epoxies with amines.[10-14] In this case, the influence of the reaction products on the reaction rate is given by the term $k_2 \alpha^m$. For these systems, an alternative modeling approach based on a mechanistic model of the reaction mechanism produces the following kinetic eq. (10):

$$d\alpha/dt = (k_1 + k_2\alpha)(1 - \alpha)(B - \alpha) \qquad (6)$$

where now α is the fraction of epoxide reacted at time t, and B, the initial ratio of amine to epoxide functional groups. It is evident that eq. (6) coincides with eq. (5) when $B = 1$ and the epoxy–amine addition is the only reaction occurring during the cure. In this case, eq. (5) represents both modeling approaches with **n** $= 2$ and **m** $= 1$. Furthermore, other nonautocatalytic complex processes can also be represented by the same model. For example, the polymerization of unsaturated polyester matrices, characterized by induction times, have been often described with a model similar to eq. (5).[4,7,12] Nonautocatalytic processes that can also be described by eq. (5) models include some simultaneous and consecutive reactions and processes characterized by a phase change of one of the reactives.

Several methods have been proposed in the literature to compute eq. (5) parameters from experimental data.[11-13] Ryan and Dutta[11] proposed a numerical method based on the analysis of the initial reaction rate and on the maximum of the reaction rate curve. The method has been successfully applied to model the cure behavior of epoxy
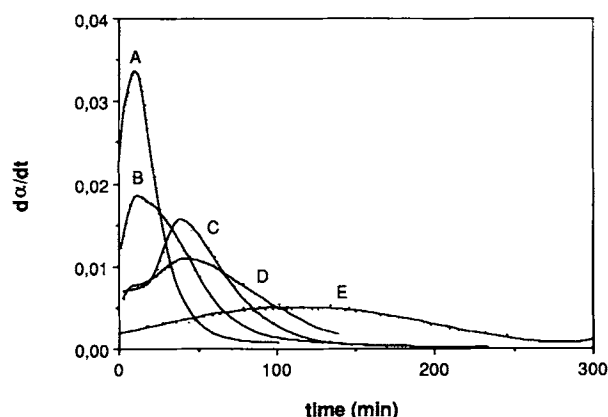
Figure 1   Isothermal DSC experiments of REX 378 at (A) 230°C, (B) 215°C, (C) 210°C, (D) 200°C, and (E) 180°C.

systems. However, to allow analytical calculations, they assumed that the total reaction order was two (**m** + **n** = 2), restraining the range of application of the proposed analysis. Good results were also obtained by Moroni et al.[13] on the calculat on of eq. (5) parameters by nonlinear regression analysis; but the same assumption that **m** + **n** = 2 was included in the analysis, limiting the application of the computing method. New powerful computer packages for statistical analysis can also be applied to determine model parameters. However, the application of these mathematical tools generally requires an accurate choice of an initial guess of the computing parameters and does not give the possibility to visualize the quality of the experimental data as in traditional graphic methods. In this paper, we propose a graphic–analytical method to compute the parameters of autocatalytic-like kinetic models represented by eq. (5). The method, applied to the polymerization of a dicyanate matrix for high-performance composites, does not include any assumption on the total reaction order.

EXPERIMENTAL

A dicyanate prepolymer (AROCY REX 378) recently developed by Hi-Tek Polymers Inc. as a potential matrix for composites used in radome aircraft structures or circuit board applications has been analyzed to illustrate the approach presented here. The basic chemical structure of AROCY REX 378 is given elsewhere.[15]

Experimental measurements were carried out using a TA Instruments differential scanning calorimeter (DSC Model 912) interfaced to a TA 2000 controller. Several isothermal experiments were conducted in the temperature range of 180–250°C. The residual heat of reaction measured in dynamic runs performed on previously cured samples was used to verify that a nonsignificant amount

of polymerization was lost during start up in isothermal tests. The total heat associated with the curing reaction (H_{ult}) was measured in nonisothermal DSC tests performed at temperature conditions (30–400°C) that guarantee reaction completion. More experimental details are given elsewhere.[16]

RESULTS AND DISCUSSION

The results of the complete kinetic characterization of the dycianate resin have been reported previously.[16] In this work, we report the methodology developed to compute the parameters of the cure kinetic model using isothermal DSC test results. Isothermal DSC thermograms expressed in terms of reaction rate as a function of time for the dicyanate matrix are shown in Figure 1. The nonzero initial reaction rate characterizes all the experimental curves, suggesting an autocatalytic kinetic behavior represented by the eq. (5) model. Moreover, the thermogram peak is shifted at longer times at lower test temperatures.

To develop the kinetic model, the main assumption that the cure mechanism is the same over all the temperature range studied is usually made.[7-14] Then, following the eq. (5) model, the constant k_1 was graphically calculated as the initial reaction rate at $\alpha = 0$, given by the intercept of the thermogram curves of Figure 1. The list of k_1 values is given in Table I.

To obtain a first guess of the reaction order **n**, eq. (5) has been modified in the following form:

$$\ln(d\alpha/dt) = \ln(k_1 + k_2\alpha^m) + n\ln(1 - \alpha) \qquad (7)$$

The representation of $\ln(d\alpha/dt)$ as a function of $\ln(1 - \alpha)$ is shown in Figure 2 (right line) for one of the isothermal experiments. By inspection of eq. (7), it is possible to conclude that the slope of the linear behavior observed when $\alpha \rightarrow 1$ is the reaction order **n**. Equation (5) can be also rearranged in a different form:

$$\ln\{[(d\alpha/dt)/(1 - \alpha)^n] - k_1]\} = \ln k_2 + m\ln\alpha \qquad (8)$$

The representation of the first term of eq. (8), calculated

Table I   Kinetic Parameters of the Autocatalytic Model Obtained from each Isothermal Test Performed with DSC

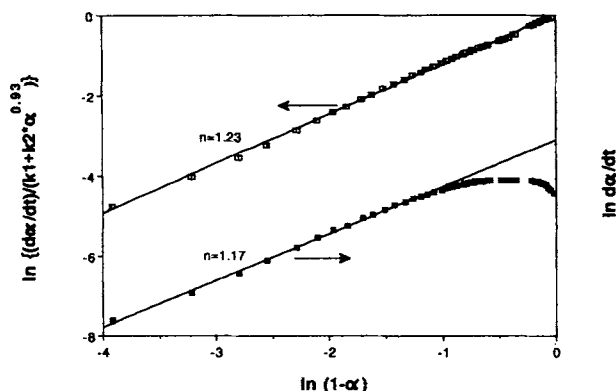| $T(K)$	$\mathrm{Ln}(k_1)$	$\mathrm{Ln}(k_2)$	n	m
453	−6.215	−4.189	0.88	1.05
473	−5.521	−3.572	1.16	1.0
483	−5.036	−3.202	1.06	1.18
488	−4.506	−3.014	1.25	0.95
493	−4.492	−3.037	1.25	0.83
503	−3.863	−2.278	1.41	0.89

Figure 2 Graphic representation of eqs. (7) and (9) for isothermal DSC results obtained at 215°C: computation of reaction order **n**.

using previously computed k_1 and **n** values, is given in Figure 3 as a function of ln α for the same isothermal experimental results shown in Figure 2. A linear behavior in almost the whole range is observed given the possibility to calculate the reaction order **m** and the kinetic constant k_2, respectively, as the slope and intercept of the straight portion of the graphic representation.

Applying the described procedure, a first set of parameter values was obtained. However, to obtain more precise values, an iterative procedure can be applied. Equation (5) can be rearranged again to give

$$\ln(d\alpha/dt) - \ln(k_2\alpha^m + k_1) = n \ln(1 - \alpha) \qquad (9)$$

After k_2 and **m** are evaluated using eq. (8), the left part of eq. (9) can be calculated and plotted as a function of $\ln(1 - \alpha)$. A neat linear behavior, in the whole range analyzed, is represented in Figure 2 (left line) for the same experimental results used before. The new value of the
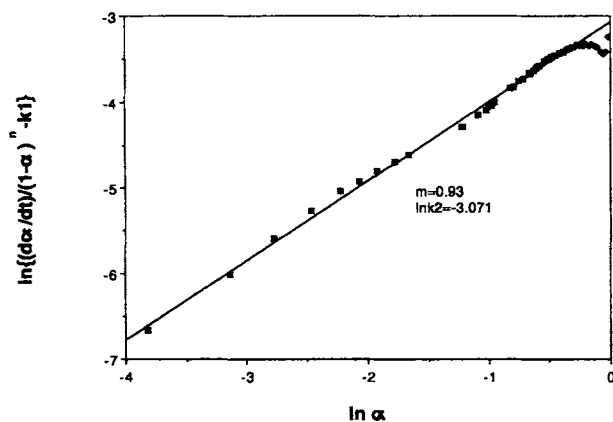

Figure 3 Graphic representation of eq. (8) for isothermal DSC results obtained at 215°C: computation of reaction order **m** and ln k_2.
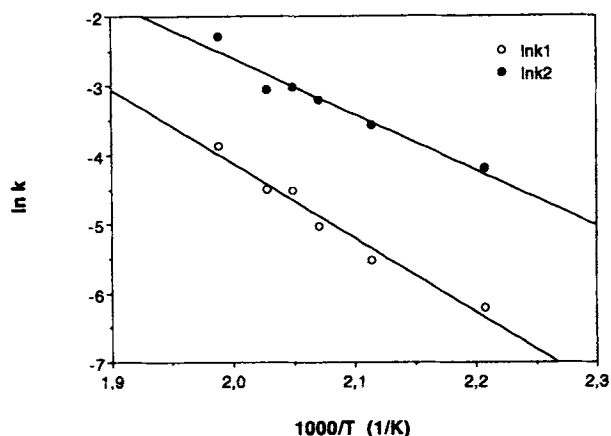

Figure 4 Temperature dependence of rate constants k_1 and k_2: determination of the activation energies E_1 and E_2.

reaction order **n** obtained from the slope is close to the one obtained previously. Now eq. (8) can be applied again to obtain new values of **m** and k_2 (**m** = 0.94, ln k_2 = −3.014) that are very close to the previous ones. This iterative procedure was repeated until convergence of **n** and **m** values within a preset interval. Normally, two or three iterations were enough to obtain values with less than 1% difference between subsequent calculations.

The values of the four eq. (5) parameters obtained by this procedure are reported in Table I. No correlation between the dispersion of values of the reaction orders and test temperature was observed. Indeed, the assumption made that the cure mechanism is the same over the entire temperature range analyzed implies that the reaction orders should be constant. Then, average values of all the isothermal experiments were calculated, giving **m** = 0.98 and **n** = 1.12. It is interesting to note that the total reaction order (**m** + **n**) results are of the order of 2 as assumed for different thermoset polymerization reactions by other authors. The utility of the proposed method is highlighted if the controversy between mechanistic models (**m** + **n** = 3 for B = 1) and the commonly used empirical models (**m** + **n** = 2)[11-13] is considered. In our case, no assumption on the value of the total reaction order was made in advance and best-fitting values of **m** and **n** were obtained.

Furthermore, assuming that k_1 and k_2 are a function of temperature and follow the Arrhenius-type behavior

Table II General Kinetic Parameters of the Autocatalytic Model

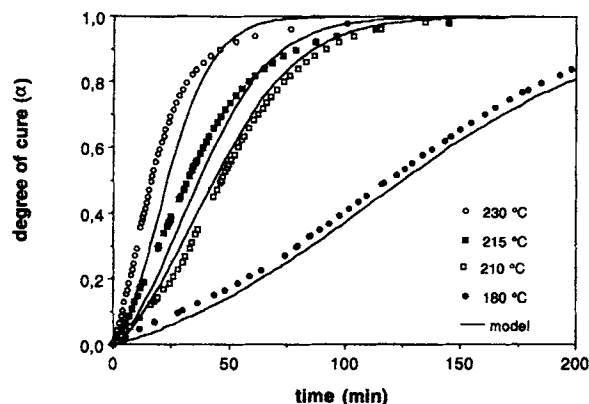| |
| --- |
| ln k_1 = 14.53 (ln 1/s) |
| ln k_2 = 10.34 (ln 1/s) |
| E_1 = 77.74 KJ/mol |
| E_2 = 54.54 KJ/mol |
| m = 0.98 |
| n = 1.12 |

Figure 5 Comparison between model predictions and experimental results obtained in isothermal DSC tests at different temperatures.

reported in eq. (4), their respective activation energies can be calculated from the plot of $\ln k_1(T)$ and $k_2(T)$ as function of $1/T$ as shown in Figure 4. A quite linear behavior was obtained allowing the calculation of the activation energies for both kinetic constants and confirming the consistency of the applied procedure. The average value of the four parameters of the autocatalytic model represented by eq. (5) are listed in Table II.

The developed model and the obtained parameters were used to predict the behavior of the reacting system under different isothermal processing conditions. A good agreement between predictions of the model and experimental data, expressed as degree of cure as a function of time for the different temperatures analyzed, is reported in Figure 5, confirming the ability of the developed model to represent the behavior of the studied dicyanate matrix and of the method proposed to determine the model parameters.

CONCLUSIONS

A simple method to calculate the parameters of the autocatalytic-like kinetic model of the cure of a thermoset has been proposed and verified experimentally. The method, based on graphic analysis of isothermal DSC test results, has been applied to develop a kinetic model for the polymerization reaction of a thermosetting dicyanate polymer used as a matrix of high-performance composite polymers. The model and the method presented here are useful tools to be applied for design, optimization, and control of the processing of thermoset-based high-performance composites.

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