Resin Transfer Molding (RTM) Process of a High Performance Epoxy Resin. I: Kinetic Studies of Cure Reaction

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The cure kinetics of a high performance PR500 epoxy resin in the temperature range of 160–197°C for the resin transfer molding (RTM) process have been investigated. The thermal analysis of the curing kinetics of PR500 resin was carried out by differential scanning calorimetry (DSC), with the ultimate heat of reaction measured in the dynamic mode and the rate of cure reaction and the degree of cure being determined under isothermal conditions. A modified Kamal's kinetic model was adapted to describe the autocatalytic and diffusion-controlled curing behavior of the resin. A reasonable agreement between the experimental data and the kinetic model has been obtained over the whole processing temperature range, including the mold filling and the final curing stages of the RTM process.

INTRODUCTION

Fiber reinforced polymer composites have been frequently used as construction materials in the aerospace and the automotive industries (1, 2). One of the processes for fabricating these fiber reinforced polymer composites is resin transfer molding (RTM). RTM's several advantages include production consistency, cost reduction, and reduced cycle time over conventional hand lay-up of prepreg and the autoclave curing process. RTM therefore has become a promising fabrication technology for producing large and high performance composites in the aerospace industry (3). The RTM process involves the injection of a low viscosity pre-catalyzed thermosetting resin, under pressure and/or vacuum, into a heated mold cavity containing a pre-placed fiber preform and the subsequent curing of the resin to form a composite part. During mold filling, the fiber preform is saturated with a resin having an increasing viscosity due to the curing reaction. After the fiber preform is completely saturated with resin, the curing of the resin is accelerated past its gel point to form a crosslinked polymer network. The entire process is heated according to the cure kinetics of the resin. To date, most of the investigations on RTM processes reported have been on resin flow through a porous medium during processing (4–6). However, very little consideration was taken of the chemical reaction of high performance epoxy resin during the filling stage, which is one of the most important parameters in optimizing the process for fabricating large advanced composites. As a consequence, the ability to predict and to monitor the kinetic behavior of resin during the impregnation (filling) phase is an important part of the development and the control of resin transfer molding processes.

A variety of kinetic models have been used to relate the rate of the chemical reactions to time, temperature, and the degree of cure, as described in a review paper by Halley *et al.* (7). General models for the description of the reaction kinetics of epoxy matrix during the autoclave processing of thermoset based composites have been proposed. For example, Kamal *et al.* (8), Dusi *et al.* (9), and Kenny *et al.* (10) introduced modifications accounting for limiting curing and diffusion-controlled behavior in the model describing the curing of epoxy. Later, Barral *et al.* (11) employed Kamal's (8) autocatalytic model with a diffusion factor to describe the isothermal cure kinetics of amine cured epoxy resin. However, they focused on the description of the curing process during autoclave molding. To our knowledge, a model that can accurately describe the cure kinetics of the high performance epoxy in the filling stage of RTM processing is still lacking.

In this paper the cure kinetics of a high performance one-part epoxy-amine resin, PR500, has been studied for being used in evaluating the resin processability in

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Table 1. Properties of PR500 Resin.

3M PR500 epoxy resin is an one part resin containing a mixture of diglycidyl ethers of ortho-substituted-4-hydroxy-phenylfluorene base resin and 9,9-bis (aminophenyl) fluorene hardener.	
Properties	**Properties**
Viscosity (mPa · s) at 25°C	thick paste, very high
Minimum viscosity (mPa · s) at 160°C	219
Reference time (min.) to 500 mPa · s at 160°C	30
Gel time (min.) at 177°C	68.5
Cured neat resin data*:	
Specific gravity of cured resin	1.25
Tensile strength (MPa)	56.6
Tensile modulus (GPa)	3.6
Tensile strain (%)	1.9
Poission's ratio	0.37
Glass transition temperature (°C)	200
Equilibrium moisture weight gain (%)	1.56
(In the 100% R.H., 88°C environment)	

*From 3M data sheet.

RTM processes. Specifically, an empirical expression based on Kamal's kinetic model was adapted to describe the autocatalytic and diffusion controlled curing behavior of resin over the whole processing temperature range, including the mold filling and the final curing stages of RTM processes.

EXPERIMENTAL

Materials

The epoxy resin studied was PR500 resin, obtained from 3M Co., which is a one-part tough epoxy resin specially designed for resin transfer molding. It consists

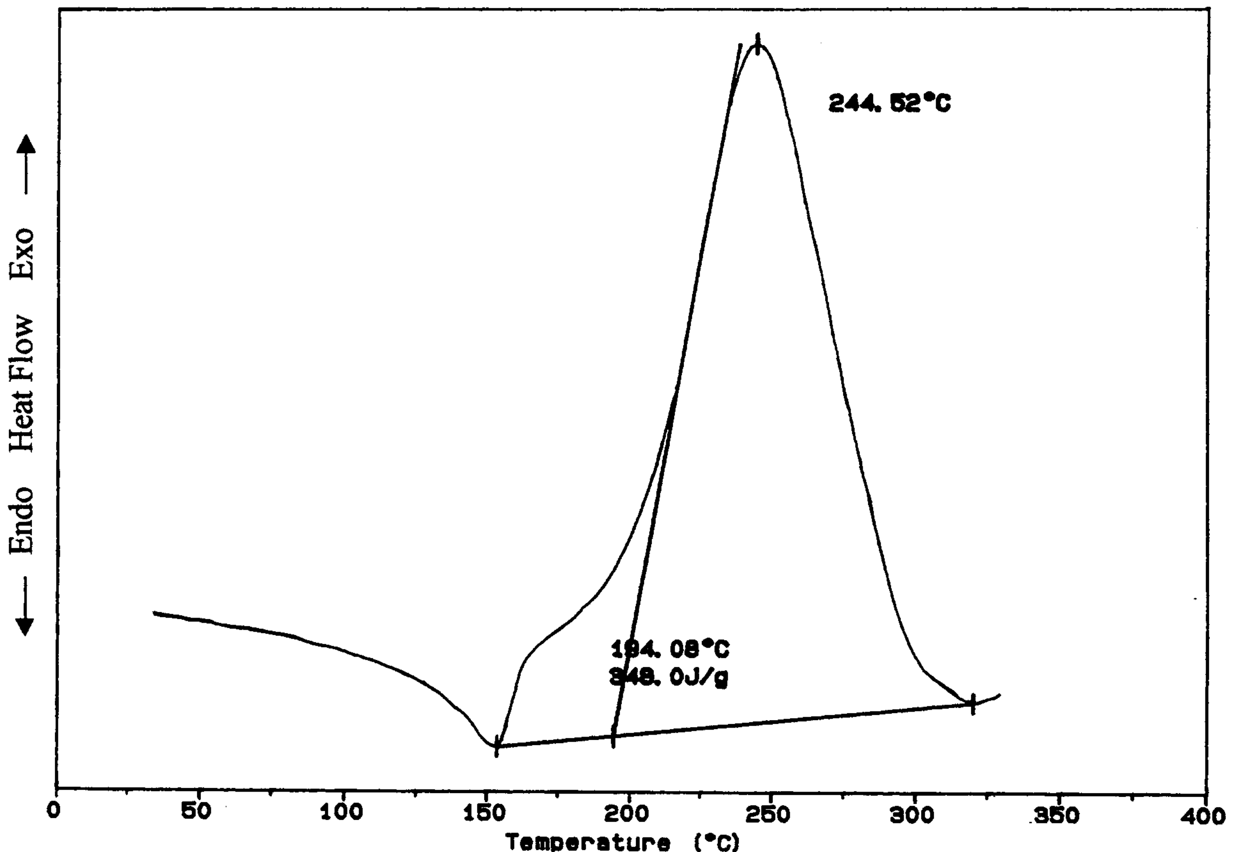

Fig. 1. DSC thermogram in dynamic mode at a heating rate of 10°C/min.

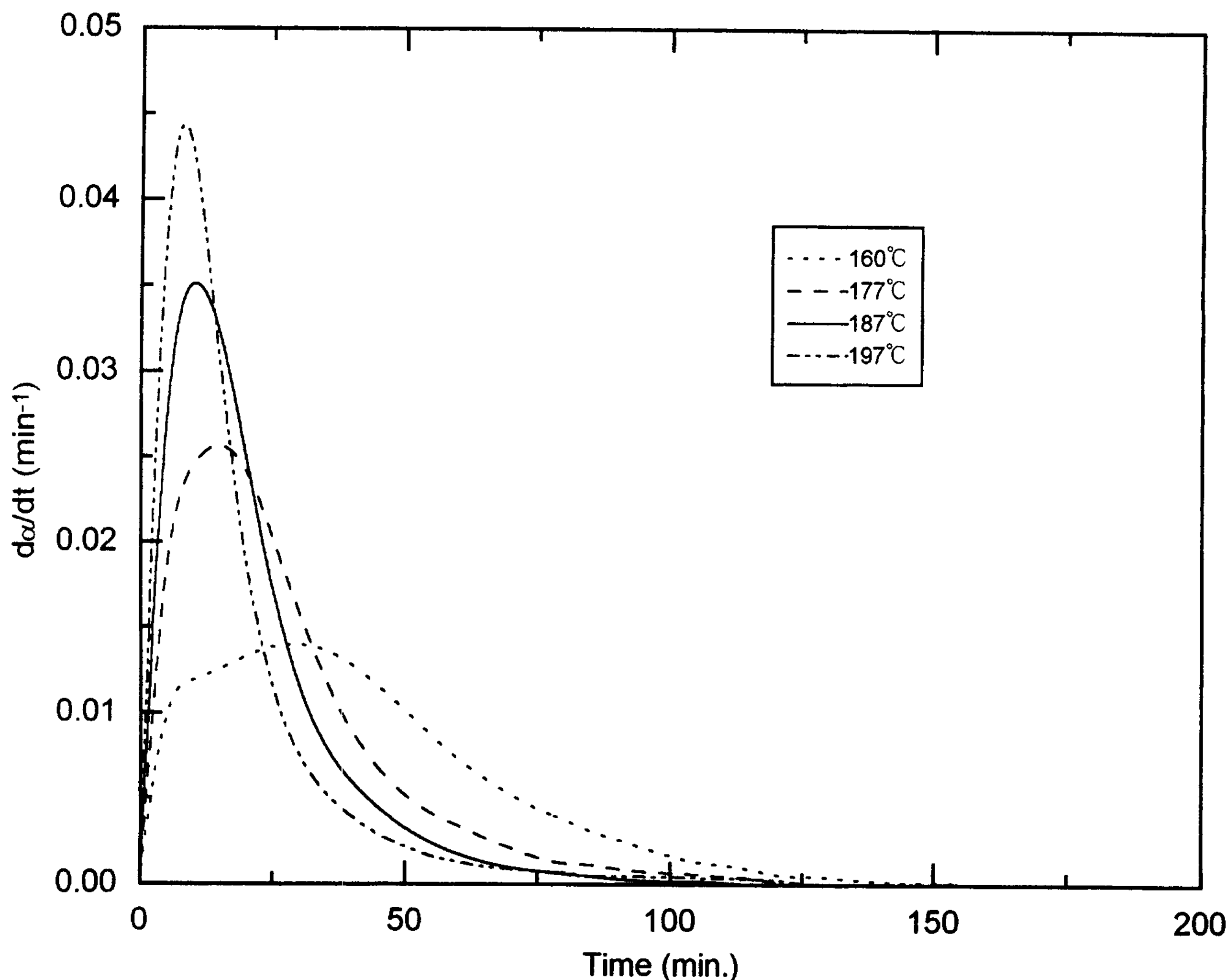

Fig. 2. Reaction rate, dα/dt, as a function of time at different temperatures.

Table 2. Temperature Dependence of Reaction Order *n* and Maximum Degree of Cure, α_{MAX}.

Temperature (°C)	Reaction Order *n*	α_{MAX}
150	—	0.804
160	1.0	0.948
177	1.13	0.955
187	1.22	0 968
197	1.33	0.965

of premixed diglycidyl ethers of ortho-substituted-4-hydroxy-phenylflorenes matrix resin with 9,9-bis (aminophenyl) fluorene curing agent. The fluorene, a tricyclic hydrocarbon group, in the backbone of the polymer with low crosslink density causes a high glass transition temperature above 200°C. This fluorene containing resin and the curing agent improved the toughness and the hot/wet durability of the resin (12, 13). A brief characterization of the resin is summarized in *Table 1*.

Thermal Analysis

A DuPont Model 2910 Differential Scanning Calorimetry (DSC) and a TA Instruments Thermal Analyzer 2100 system were used to measure the heat of reaction, the rate of cure and the degree of cure of PR500 epoxy-amine resin. The analysis was conducted by assuming a linear proportionality between the heat evolved during the cure and the degree of cure. Both dynamic and isothermal experiments were performed to monitor the cure reaction. Samples of 5–20 mg weight were sealed in hermetic pans and were heated from 25 to 350°C at rates of 2, 5, 7.5, 10, and 20°C/min. The ultimate heat associated with the curing reaction was measured in the dynamic DSC experiments. Isothermal DSC experiments were performed at temperatures of 150°C, 160°C, 177°C, 187°C, and 197°C.

RESULTS AND DISCUSSION

The DSC thermogram for dynamic cure of PR500 resin at a heating rate of 10°C/min is shown in *Fig. 1*.

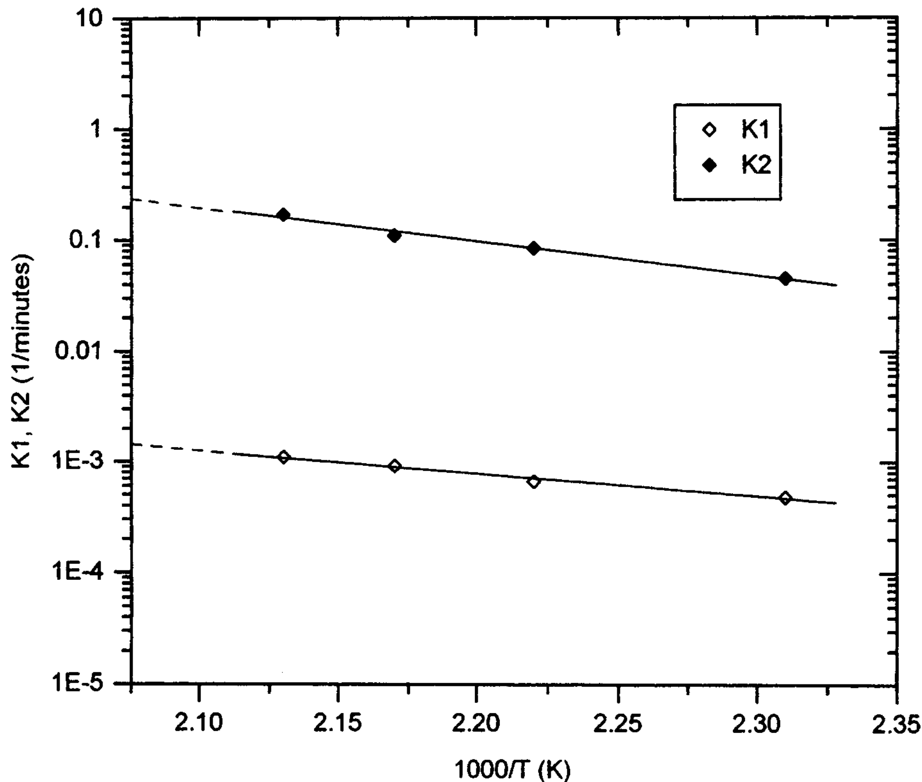

Fig. 3. Arrhenius plot of rate constants, k_1 *and* k_2.

In *Fig. 1*, there is a small reproducible endothermic peak around 155°C immediately followed by the onset of the cure exotherm. This small endothermic peak at 155°C resulted from the melting of the amine hardeners premixed in the resin. The cure curve of this epoxy-amine resin displayed a single exothermic peak, which had an onset point of 194°C, and the peak cure temperature occurred at 244.5°C. In the curing reaction, the ultimate heat of reaction, H_U, is defined as the total heat generated during the curing reaction. The average value of H_U obtained from five scans of different heating rate was found to be 343.5 ± 5.6 J/g. Assuming the cure reaction is only a thermal event, then the reaction rate $d\alpha/dt$ is directly proportional to the rate of heat generation dH/dt. It is possible to evaluate the reaction rate $d\alpha/dt$ at the time t and the degree of cure α reached in time t by means of the following expressions (14):

$$\frac{d\alpha}{dt} = \frac{1}{H_U}\left(\frac{dH}{dt}\right)_t \quad (1)$$

$$\alpha = \frac{\Delta H_t}{H_U} \quad (2)$$

Where the rate of heat generation $(dH/dt)_t$ is directly the calorimetric signal at a time t, H_U is the ultimate heat of reaction associated with the complete conversion of all the reactive groups, and ΔH_t is the heat released until the time t, and can be obtained directly by integration of the calorimetric signal dH/dt until time t. The reaction rate, $d\alpha/dt$, as a function of time for PR500 resin at four different curing temperatures is presented in *Fig. 2*. In *Fig. 2*, an increase in temperature facilitates the curing reaction. Moreover, a maximum of the reaction rate occurred at some point other than the starting point, indicating that the nature of the reaction is autocatalytic. The total amount of heat generated at a constant temperature was defined as the isothermal heat of reaction, H_T. Since the latter half of the curing of an epoxy-amine resin is often diffusion controlled, the cure reaction will reach a plateau before a full degree of cure is reached. Incomplete reactions obtained during isothermal processes are caused by vitrification, which dramatically reduce the mobility of the molecules. The vitrification occurs when the glass transition temperature (Tg) approaches the curing temperature. The maximum degree of cure of the resin is therefore temperature dependent up to a temperature that is high enough to provide sufficient molecular mobility for reaction. Thus, the maximum degree of cure α_{max} is defined by the ratio of H_T to H_U (15, 16) and can be determined by an isothermal DSC test. As given in *Table 2*, the α_{max} was found to be less than unity between 160°C and 197°C, which is a typical temperature range for RTM processing. It is worthwhile to note that the reaction rate is extremely slow and the maximum degree of cure is only 0.804 at 150°C, which is below the melting temperature of hardener premixed in the PR500 resin. A linear empirical temperature dependent relation can be obtained to show the dependence of the maximum

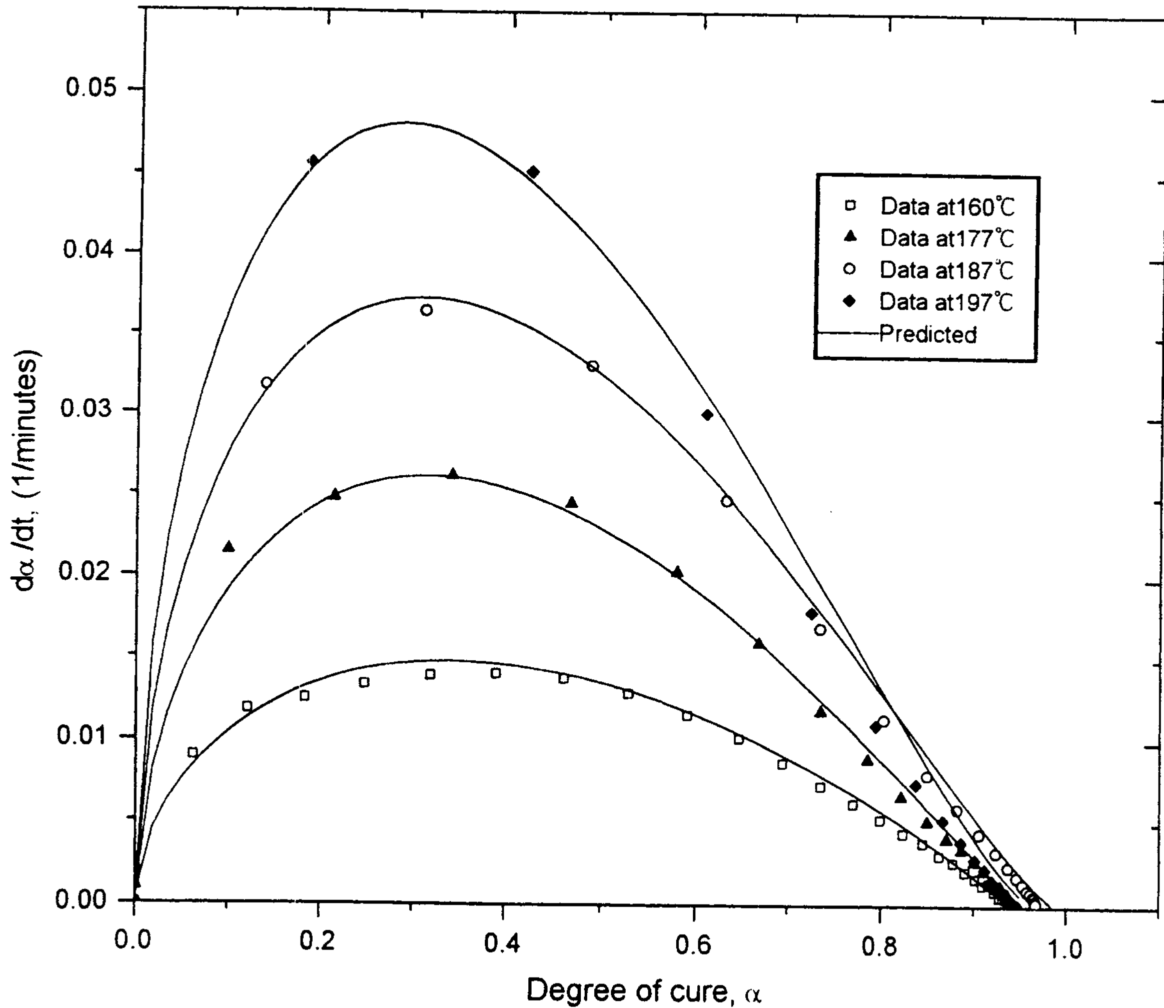

Fig. 4. Comparisons of experimental data with predictions: reaction rate, dα/dt, vs. degree of cure, α at different temperatures.

degree of cure, α_{max} on temperature in the temperature range of 160–197°C, indicating the diffusion-controlled phenomena at the later stages of the cure reaction (16). This empirical relation is given in *Eq 3*.

$$\alpha_{max} = 7.03T(K) + 0.64 \quad (3)$$

Therefore, the maximum degree of cure, α_{max} was introduced into Kamal's autocatalytic kinetic model (16, 17) to characterize the curing of PR500 epoxy system by considering both autocatalytic curing at the initial stage and diffusion-controlled curing at the final stage. This model is given in the following.

$$\frac{d\alpha}{dt} = (K_1 + K_2\alpha^m)(\alpha_{max} - \alpha)^n \quad (4)$$

The reaction constant K_1 and K_2 are the temperature-dependent parameters, which are given by Arrhenius expressions,

$$K_1 = A_1 \exp\left(-\frac{E_1}{RT}\right)$$
$$K_2 = A_2 \exp\left(-\frac{E_2}{RT}\right) \quad (5)$$

where A_1 and A_2 are the pre-exponential factors, E_1 and E_2 are the activation energies, R is the universal gas constant, and T is the absolute temperature in degrees Kelvin.

The parameters m, n, K_1, and K_2 were estimated without any constraints on them by fitting the experimental data shown in *Fig. 4* to *Eq 4* using a nonlinear regression method. The obtained value of m is 0.57. However, the value of n in *Table 2* exhibited a linear dependence on the reaction temperature in the following form:

$$n = -3.01 + 0.00923^{*}\, T(K) \quad (6)$$

Rate constants K_1 and K_2 are shown as a function of inverse temperature in *Fig. 3*. In *Fig. 3*, the values of A_1, A_2, E_1, and E_2 in *Eq 5* were determined from the intercepts and the slopes of these lines, and they are 22.33 min^{-1}, 6.14 × 10^5 min^{-1}, 38.7 KJ/mole, and 59.2 KJ/mole, respectively. Thus, the curing behavior of PR500 resin can be described by the following equation.

$$\frac{d\alpha}{dt} = \left(22.33\exp\left(-\frac{4.66^{*}10^{3}}{T}\right) + 6.14^{*}\ 10^{5}\exp\left(-\frac{7.12^{*}10^{3}}{T}\right)\alpha^{0.57}\right)(\alpha_{max} - \alpha)^{(-3.01+0.00923^{*}T)} \tag{7}$$

The comparisons between experimental data and empirical predictions by *Eq 7* in $d\alpha/dt$ as a function of α over the temperature range of 160–197°C are presented in *Fig. 4*. A reasonably good agreement was obtained in *Fig. 4*. In addition, a maximum reaction rate occurring at about 30°C of degree of cure by autocatalytic reactions was observed, as shown in *Fig. 4*.

CONCLUSIONS

The kinetic behavior of high performance PR500 epoxy resin has been studied for mold filling and the final curing stages of resin transfer molding. An adapted Kamal's model with added curves fit for the reaction order n and the maximum degree of cure α_{MAX} as a function of temperature was obtained. This model is used to account for both the autocatalytic and the diffusion-controlled step in the epoxy-amine curing process. Kinetic rate constants and the activation energy associated with the cure reaction were also determined. The empirical model was then verified in the temperature range of 160–197°C, which is typical of RTM processing. A reasonable agreement was obtained between the predicted values from the model and the experimental cure data.

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