Curing Kinetics of Medium Reactive Unsaturated Polyester Resin Used for Liquid Composite Molding Process

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ABSTRACT: The cure kinetics of medium reactivity unsaturated polyester resin formulated for Liquid Composite Molding process simulation was studied by Differential Scanning Calorimetry (DSC) under isothermal conditions over a specific range of temperature. For isothermal curing reactions performed at 100, 110, and 120°C, several influencing factors were evaluated using the heat evolution behavior of curing process. We propose two- and three-parameter kinetic models to describe the cure kinetics of thermoset resins. Comparisons of the model solutions with our experimental data showed that the three-parameter model was the lowest parameter model capable of capturing both the degree of cure and the curing rate qualitatively and quantitatively. The model parameters were evaluated by a non-linear multiple regression method and the temperature dependence of the kinetic rate constants thus obtained has been determined by fitting to the Arrhenius equation. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 2415–2420, 2009

Key words: unsaturated polyester resin; curing of polymers; differential scanning calorimetry (DSC); kinetics modeling; activation energy

INTRODUCTION

Liquid Composite Molding (LCM) is an important technology for producing complex and large composite structures. Development of a proper LCM manufacturing process requires a proper mold design, a successful injection strategy and a well-defined cure cycle. Optimization of LCM process parameters based on trial and error is both expensive and time consuming. Researchers have employed computer simulation models as a design tool for the development of LCM process and to optimize the process parameters.[1–4] Resin curing characterization is one of the most important requirements for a realistic LCM process simulation. The establishment of cure kinetics provides valuable information to design the cure and post cure cycles, which are the prerequisites for optimizing the process parameters and improving the quality of the final product.

Unsaturated Polyester (UP) resin is one of the most popular thermosetting matrices used in advanced polymeric composite structures because of its good processing characteristics, specific physical properties, moderate price, and its ability to cure under normal temperature and pressure and during heating and compression. The curing of a UP resin is a free radical polymerization that is highly exothermic in nature in which the resin is transferred from liquid state into a rigid cross-linked molecular structure that becomes insoluble and infusible. In general, UP resins are classified into high, medium, and slow reactive depending on the density of reacting sites that are tailored to suit different applications such as Hand Lay-up, LCM processes, and Pultrusion process. However, the choice of particular reactivity UP resin for a particular manufacturing process depends on a balance between wetting time and cure time. The slow reactivity UP resin is preferred for Hand Lay-up process as its process time typically ranges from several minutes to hours, whereas medium reactivity UP resin is preferred for LCM processes since its process time falls in the order of minutes.

Experimental techniques such as Differential Scanning Calorimetry (DSC)[5–26] and Fourier Transform Infrared Spectroscopy (FTIR)[27–31] have been employed to study the curing reaction kinetics of thermosetting polymers. DSC is the most commonly used experimental technique to measure the amount of heat generated during curing reaction. Isothermal cure studies[5–13] and dynamic heating experiments[14–26] are the two different approaches to determine the cure kinetics of a thermosetting resin. Of these, isothermal mode is often preferred because of its ability to mimic the actual processing conditions used to generate the final thermoset product, and also because it provides the rate of heat generation as a function of time without the occurrence of thermal gradients during cure analysis.[7]

Modeling of cure kinetics quantifies the thermal and temporal effects on the degree of cure of

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thermosetting resin. A variety of kinetics models have been developed in the literature to quantify the dynamics of cure rate and cure conversion. In general, these models can be classified into two categories, namely mechanistic kinetic models[11,12,19–22,24] and the phenomenological or empirical models.[6–10,13–18,23] The mechanistic models attempt to quantify the balance of chemical species taking part in the cure reaction by using a mathematical function that relate the reaction rate path to cure time and temperature. Phenomenological or empirical kinetic models are simple mathematical expressions, which are easier to handle in compare with mechanistic models. Several empirical models have been suggested to describe the curing reaction of different thermosetting matrices like polyester,[13–16] epoxy,[8–10,18] and phenolic resins.[26]

A few empirical forms of the reaction model have been suggested by the researchers, the simplest being an nth order two-parameter rate equation[5–7,9,10,16,26] given by

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

where n is the reaction order, α is the conversion or the degree of cure, and k is the cure rate constant defined by an Arrhenius expression,

$$k(T) = Ae^{-(E/RT)}, \tag{2}$$

where E is the activation energy, A is the pre-exponential factor, R is the gas constant (8.314 J/mol K), and T is the absolute temperature (K).

The nth order rate model given by eq. (1) predicts that the reaction rate peaks at the beginning of curing. However, this model fails for resin systems following autocatalytic kinetics which attain a maximum reaction rate at some intermediate degree of cure. For such autocatalytic isothermal cure processes, a kinetic model was proposed by Kamal and Sourour,[7,9,13,18] which is given by

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1-\alpha)^n, \tag{3}$$

where k_1 and k_2 are the rate constants, α is the conversion or the degree of cure, and m and n are the reaction orders of the four parameter model given by eq. (3). However, Kamal and Sourour's model does not consider incomplete cure reaction, and it fails at the latter stages of the reaction. Some investigators have considered the case of incomplete reaction by modifying the form of Kamal and Sourour's model[9,10,18] as

$$\frac{d\alpha}{dt} = k\alpha^m(1-\alpha)^n. \tag{4}$$

However, detailed studies on specific resin systems particularly designed for typical LCM applica-
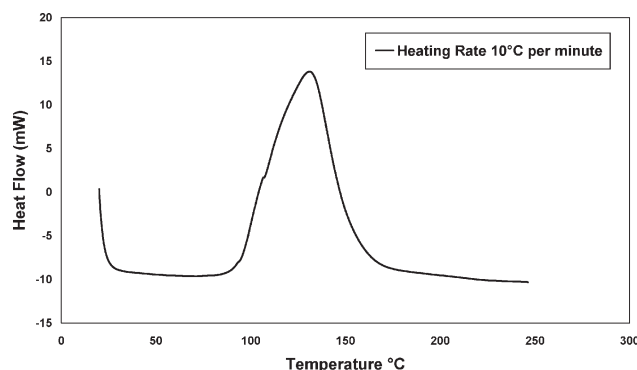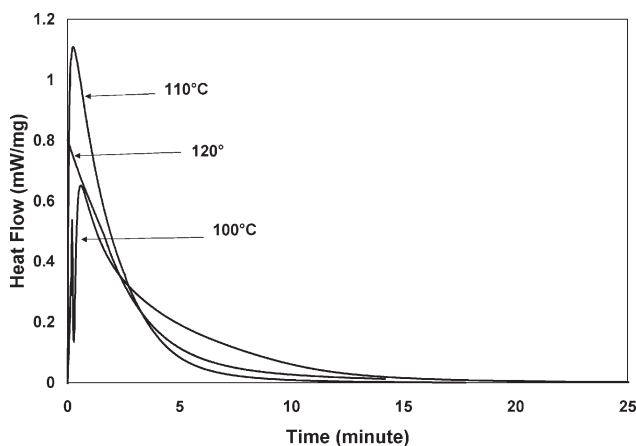
Figure 1 Dynamic heat flow curve of a medium reactive UP resin curing at different temperatures.

tions could not be found in the literature. In this study, the cure kinetics of medium reactive UP resin, which is the most widely used resin for LCM process, was investigated. Medium reactive UP resin have faster rate of heat generation and higher peak exotherm as compared to low reactive resin systems. Similarly, high reactive resins have faster rate of heat generation and higher peak exotherm as compared with medium reactive resins. The experimental analysis at our laboratory shows a typical exotherm range of 130 to 150°C, 150 to 180°C, 180 to 210°C for low, medium, and high reactivity UP resins, respectively.

This work attempts to obtain the reaction kinetics data at three different isothermal temperatures using DSC and proposes a new low-parameter empirical model to describe the cure kinetics as a function of time and temperature, which are the two variables necessary to simulate the resin curing during LCM process. Comparisons of our model with our experimental data reveal that the model is capable of predicting the reaction kinetics satisfactorily over the range of temperature and time studied. This article is organized as follows: first, the DSC dynamic scan and isothermal DSC measurements are analyzed to convert the raw thermal data to the degree of cure and the rate of cure. Then, the experimentally obtained data for the above two variables are fitted to our proposed two models to obtain the kinetic parameters of the model.

EXPERIMENTAL METHOD

The sample was prepared by mixing medium reactive UP resin, cobalt nitrate (which acts as accelerator), and methyl ethyl ketone peroxide (which act as catalyst) at 100 : 1 : 1 volume ratio. The commercially available medium reactive UP used for this study has been manufactured by using a mixture of acids such as isophthalic acid, maleic anhydride,

Figure 2 Isothermal normalized heat flow curves of a medium reactive UP resin at 100, 110, and 120°C vs cure time.

and propylene glycol to an acid value of 15 ± 2 mg KOH/g. Styrene is added to adjust the final product viscosity to 250 ± 25 cP. The DSC analysis was carried out using Pyris Diamond DSC equipment manufactured by Perkin Elmer. The curing of these samples was performed under isothermal condition and the heat flow vs. time was measured until the reaction was complete. For the required isothermal experiments, a dynamic DSC run with varying temperatures was performed. Temperatures above the onset of the reaction and below the peak heat flow were chosen for the isothermal cure study. The heat flow vs. time was measured at these temperatures until the reaction was complete. The degree of cure $\alpha(t)$ at any time t was determined using the following equation,

$$\alpha(t) = \frac{\Delta H(t)}{\Delta H_{tot}}, \tag{5}$$

where $\Delta H(t)$ is the enthalpy of the reaction at any time t, and ΔH_{tot} is the total enthalpy of the reaction.
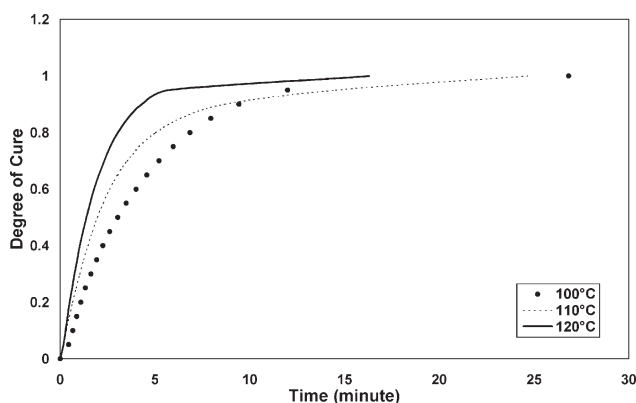
Figure 3 Degree of cure of a medium reactive UP resin at 100, 110, and 120°C vs cure time.
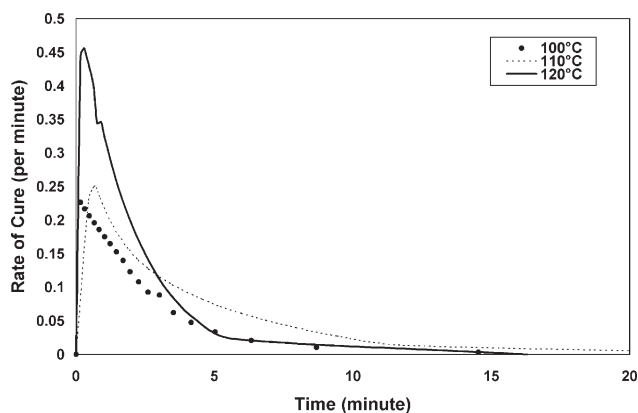
Figure 4 Rate of cure of a medium reactive UP resin at 100, 110, and 120°C vs cure time.

Modeling of cure kinetics

Typically, the cure kinetics of thermoset resin is modeled empirically with the rate of cure $\frac{d\alpha}{dt}$, given by

$$\frac{d\alpha}{dt} = k(T)^* f(\alpha), \tag{6}$$

where $k(T)$ is dependent on temperature alone and is given by eq. (2), whereas $f(\alpha)$ is dependent only on the degree of cure α.

Two-parameter model

We propose a two-parameter model for the degree of curing, which is given by

$$\alpha = \alpha_{max}(1 - e^{-kt}), \tag{7}$$

where α_{max} is the maximum degree of cure attained, t is time, and k is the temperature dependant rate constant. Differentiation of eq. (7), followed by algebraic manipulation gives the rate of cure as
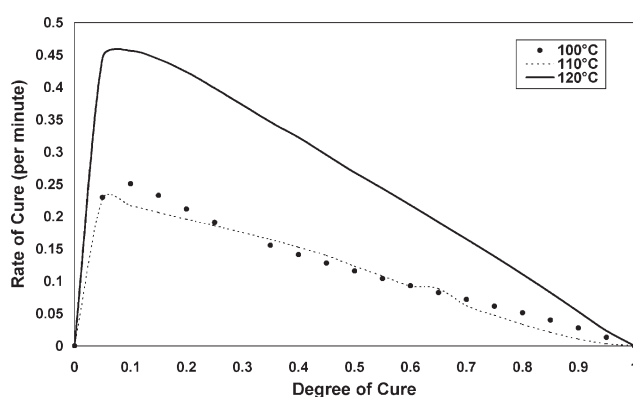
Figure 5 Experimental rate of cure versus degree of cure of a medium reactive UP resin at 100, 110, and 120°C.
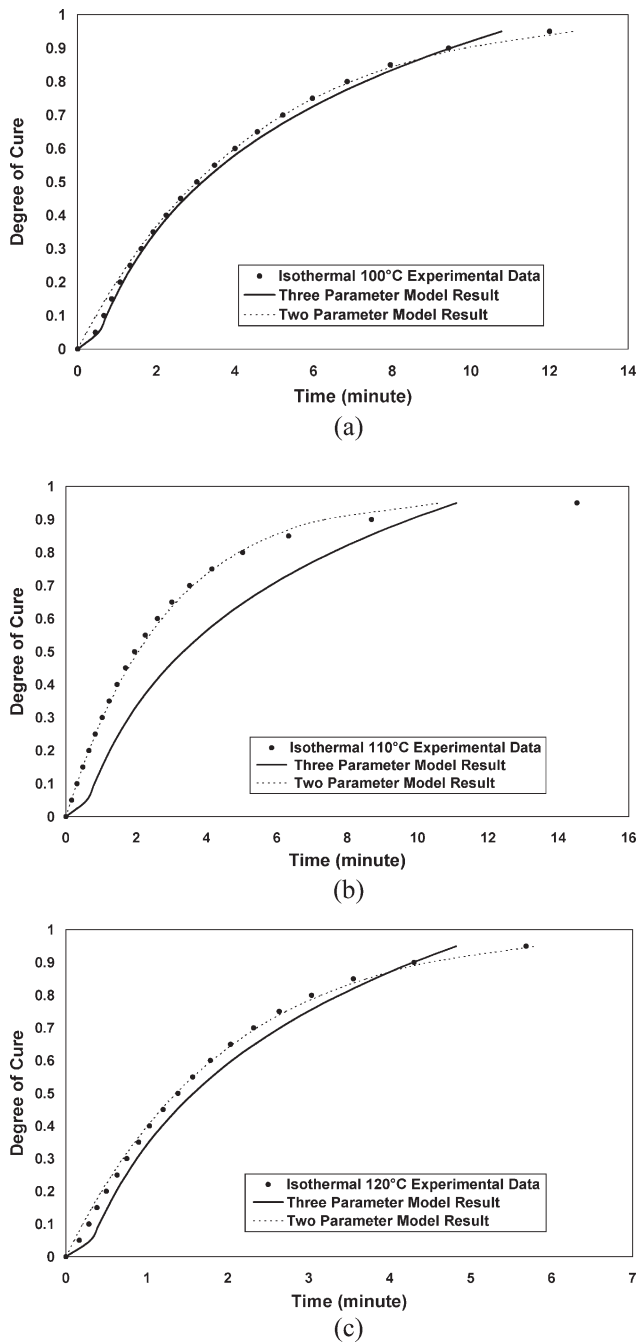
Figure 6 (a) Comparison of experimentally obtained degrees of cure at 100°C with that predicted by the models. (b) Comparison of experimentally obtained degrees of cure at 110°C with that predicted by the models. (c) Comparison of experimentally obtained degrees of cure at 120°C with that predicted by the models.
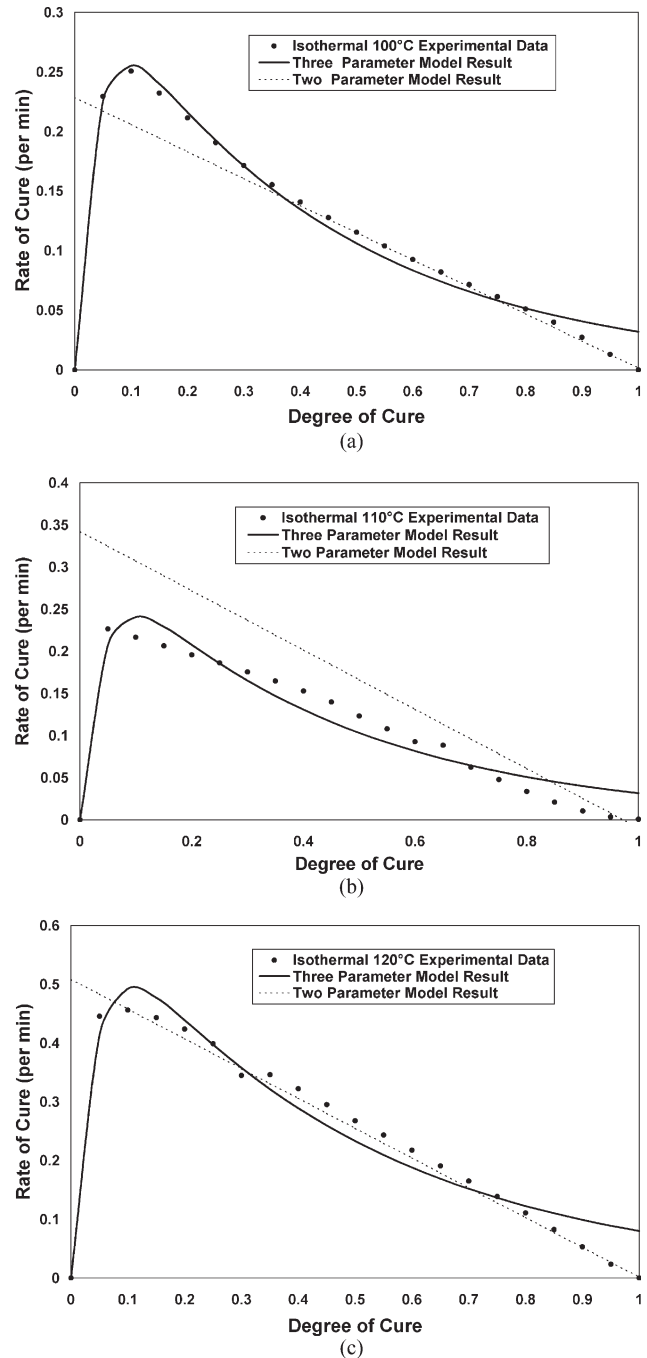
$$\frac{d\alpha}{dt} = (\alpha_{max} k)^* \left(1 - \frac{\alpha}{\alpha_{max}} \right), \qquad (8)$$

Three-parameter model

On the basis of biphasic nature of the experimentally obtained rate of cure vs. degree of cure at different temperatures (given in Fig. 7), we propose a three-parameter model capable of capturing the above dynamics, which is given by

$$\frac{d\alpha}{dt} = k(T)^* e^{-m\alpha*} Sinh(n\alpha), \qquad (9)$$

Figure 7 (a) Comparison of experimentally obtained rate of cure vs. degree of cure at 100°C with that predicted by the models. (b) Comparison of experimentally obtained rate of cure vs. degree of cure at 110°C with that predicted by the models. (c) Comparison of experimentally obtained rate of cure vs. degree of cure at 120°C with that predicted by the models.

Parameter Values for the Two-Parameter Model Obtained by Fitting to the Experimental Data

Isothermal temperature, °C	α_{max}	k Empirical rate constant, min^{-1}	Goodness of fit, $\overline{R}^2$
100	1.008	0.2269	0.9989
110	0.973	0.3520	0.9963
120	1.003	0.5073	0.9988

where m and n are reaction orders, and $k(T)$ is the temperature dependant rate constant.

RESULTS

Thermoset resin cure reaction can occur over a wide temperature range. However, a moderate cure temperature was selected to operate the DSC apparatus at an isothermal environment.

Figure 1 shows that the onset of curing reaction occurs above 90°C and the heat flow peaks around 130°C. The experimental temperature was selected between the temperature 90°C and 130°C. The reason for selecting temperature below 90°C is the reaction is too slow and it will take an appreciable time for completion, whereas above 130°C, the reaction is too fast, and a significant part of the reaction is complete before the attainment of isothermal temperatures. Three temperatures of 100, 110, and 120°C were chosen between 90 and 130°C for conducting isothermal curing experiments.

Figure 2 shows the heat flow normalized by the sample mass vs. cure time at 100, 110, and 120°C. The figure shows that the time taken to reach the peak heat flow rate decreases with increasing temperature. The total heat of reaction, ΔH_{tot}, at isothermal curing temperatures was calculated from the exotherm area under the respective normalized heat flow curves. The area under the curves from the Figure 2 shows that the total heat of reaction at different isothermal temperatures at large times are approximately same ($\Delta H_{tot} = 2.56$ mW-min/mg, 2.42 mW-min/mg, and 2.36 mW-min/mg, for 100, 110, and 120°C, respectively). The isothermal heat flow vs. time data as given in Figure 2 was numerically integrated to obtain the degree of cure using eq. (5),

which is shown in Figure 3. The experimental rate of cure is obtained simply by numerically differentiating the curves in Figure 3, which is shown in Figure 4. Figure 5 shows the cure rate vs. degree of cure at the isothermal test temperatures, obtained by using the data shown in Figures 3 and 4.

Figure 6(a–c) show the comparisons of the experimentally obtained degree of cure vs. time with that predicted by the models, whereas Figure 7(a–c) show the comparison of the experimentally obtained rate of cure vs. degree of cure with the model predictions. From Figure 6 (a–c), it is evident that at all the temperatures, the degree of cure has a steep rise in the earlier stages of the curing, and at any given time, higher the isothermal temperature, higher is the degree of cure. As can be seen from Figure 7(a–c), at a given temperature, the cure rate increases with the degree of cure and attains a maximum at $\alpha < 0.2$, then gradually decreases and finally tends to 0. It has been shown that for a given conversion, higher the isothermal temperature, higher is the cure rate. It may be mentioned that the model parameters in our two- and three-parameter models have been evaluated by using non-linear regression analysis to our experimental data; the values of the parameters for the two- and three-parameter models as well as the correlation factors for the fits are presented in Tables I and II, respectively. The temperature dependence of the kinetic rate constants of the three-parameter model (as given in Table II) has been determined by fitting to the Arrhenius equation [eq. (2)]. The frequency factor (A) and activation energy (E) have been obtained as 4.8×10^4 min^{-1} and 65.22 kJ mol^{-1}, respectively.

DISCUSSION AND CONCLUSIONS

Figure 6 (a–c) shows that the two-parameter model predicts the experimental data slightly better than the three-parameter model when the degree of cure vs. time data are compared. However, Figure 7 ac shows that the two-parameter model is incapable of capturing the qualitative nature of the experimental data as given in terms of the rate of cure vs. degree of cure. The reason for this could be attributed to the fact that the response of rate of cure vs. degree

TABLE II
Parameter Values for the Three-parameter Model Obtained by Fitting to the Experimental Data

Isothermal temperature, °C	Kinetic parameter, m	Kinetic parameter, n	k Empirical rate constant, min^{-1}	Goodness of fit, $\overline{R}^2$
100	15.3095	12.9025	0.3359	0.9063
110	14.26	11.9	0.3507	0.9354
120	13.447	11.304	0.6811	0.9491

of cure curve obtained from the experimental data is biphasic, with the ascending phase peaking at α < 0.2. However, the three-parameter model, being intrinsically biphasic in nature, can capture the biphasic nature of the experimentally obtained rate of cure vs. degree of cure data not only qualitatively but also quantitatively, and quite satisfactorily. Therefore, we conclude that the three-parameter model is the lowest parameter model that captures the curing kinetics of medium reactive UP resin, both qualitatively and quantitatively.

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