

Viscosity Modeling of a Medium Reactive Unsaturated Polyester Resin Used for Liquid Composite Molding Process

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ABSTRACT: The development of new composite product for an application through liquid composite molding (LCM) process simulation requires submodels describing the raw material characteristics. The viscosity during resin cure is the major submodel required for the effective simulation of mold-filling phase of LCM process. The viscosity of the resin system during mold filling changes as the cure reaction progresses. Applied process temperature also affects the viscosity of the resin system. Hence, a submodel describing the resin viscosity as a function of extent of cure and process temperature is required for the LCM process simulation. In this study, a correlation for viscosity during curing of medium reactive unsaturated polyester resin, which is mostly used for the LCM process, has been proposed as a function of temperature and degree of cure. The viscosity and the

degree of cure of reacting resin system at different temperatures were measured by performing isothermal rheological and isothermal differential scanning calorimetry experiments, respectively. A nonlinear-regression analysis of viscosity and degree of cure data were performed to quantify the dependence of viscosity on temperature and extent of cure reaction. Comparisons of model solutions with our experimental data showed that the proposed empirical model is capable of capturing resin viscosity as a function of extent of cure and temperature qualitatively as well as quantitatively. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 1400–1408, 2012

Key words: unsaturated polyester resin; curing of polymers; differential scanning calorimetry; viscosity modeling; liquid composite molding process

INTRODUCTION

Liquid composite molding (LCM) processes such as resin transfer molding (RTM) generally produce polymer matrix composites by injecting precatalyzed resin into mold cavities that contain reinforcement fibers. Reinforcement preforming, mold filling, and curing are the significant phases involved in the LCM process. Complete filling of the mold with adequate wetting of the fibrous media is the primary objective in RTM. Incomplete impregnation of the reinforcement perform results in defective parts, which must be scrapped. Consequently, simulation of the resin flow through the perform becomes an important step in modeling the RTM-manufacturing process. Virtual simulation of RTM involves a large number of variables related to process and product performance. Among them, rheology is the most important aspect in the mold filling of thermosetting resin in RTM as the mold fill time depends on the resin viscosity. The

resin viscosity during mold filling implicitly depends on the precatalyzed curing reaction and the process temperature. Hence, the evolution of the resin cure viscosity during mold filling are required to be quantified to the degree of cure and temperature for simulating the LCM process.^{1–3}

A number of studies have been published on the measurement of viscosity of curing-resin system under elevated isothermal temperatures, by measuring viscosity as a function of cure time.^{1,2,4–14} Researchers have used models accounting for either thermal dependency^{2,4,5,15–18} or the combination of both thermal and cure kinetics dependency^{3,14,19–21} to quantify the cure viscosity evolution up to resin gelation. Models accounting for only thermal effects have two approaches in capturing the rheological behavior of a curing-resin system. In the first approach, model quantifying the effects of temperature on viscosity was first presented, so that the parameters of the model which describes the dependence of temperature could be evaluated. The dual Arrhenius model is the best example for the aforementioned-modeling procedure, which computes only the thermal effects.^{2,8} In the second approach, the model quantifies the cure viscosity as

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a function of temperature directly.^{2,16} A variety of empirical forms of cure viscosity models have been developed by the researchers to relate the cure viscosity to a function of temperature, and curing conversion. The simplest empirical form is the Williams–Landel–Ferry (WLF) equation.^{3,6,14,15,17,21} A modified version of WLF equation was proposed by Giovanni et al.¹⁵ using the degree of cure at the gelation point. Kenny et al. developed a cure viscosity model relating the glass-transition temperature to the evolution of molecular weight.^{2,14,20} Henne et al.¹ proposed a new empirical form for the viscosity during curing based on temperature and cure conversion, as given below:

$$\eta(T^1, \alpha) = \eta_{\infty} \times \exp[(T_{\text{rheo}}/T^1) + B\alpha] \quad (1)$$

where T^1 is the temperature difference to the glass-transition temperature, T_{rheo} and B are the model parameters. An alternative simple empirical form has been proposed by Kang et al.^{2,3} using an Arrhenius form of temperature dependency as given in eq. (2):

$$\eta(T, \alpha) = \eta_0 \times \exp[(E_{\eta}/RT) + B\alpha^2] \quad (2)$$

where E is the activation energy and R is the gas constant (8.314 kJ mol⁻¹). Shanku et al.⁷ proposed an extended version of the empirical form proposed by Kang et al.:

$$\eta(T, \alpha) = \eta_0 \times \exp[(E_{\eta}/RT) + A\alpha + B\alpha^2] \quad (3)$$

where A and B are parameters depending on the temperature. Several researchers have utilized the viscosity model based on resin gelation^{2,19} in the form expressed in eq. (4).

$$\eta(T, \alpha) = \eta_0 \times \exp[E_{\eta}/RT] \times [\alpha_g/(\alpha_g - \alpha)]^{A+B\alpha} \quad (4)$$

Despite the extensive available published reports on the viscosity modeling of curing thermoset resins, detailed studies on specific resin systems particularly designed for typical LCM applications could not be found in the published reports.

The main objective of this study is to investigate the viscosity during curing of a particular medium reactive unsaturated polyester resin and to develop a mathematical model to describe the viscosity as a function of the influencing parameters. The article is structured as follows: first, the data from the isothermal rheological measurements and isothermal differential scanning calorimetry (DSC) measurements were given. In the following section, the degree of cure and viscosity as a function of cure time and temperature were reported. In the next section, the superimposed viscosity as a function of degree

of cure and temperature was shown. Finally, a correlation was developed for viscosity as a function of degree of cure and temperature and the viscosity obtained from the experiments and the correlation was compared.

MATERIALS AND METHODS

Materials

The commercially available medium reactive UP used for this study has been manufactured using a mixture of acids such as isophthalic acid, maleic anhydride, and propylene glycol to an acid value of 15 ± 2 mg KOH g⁻¹. Styrene is added to adjust the final product viscosity to 250 ± 25 cP. The reacting resin sample was prepared by mixing medium reactive unsaturated polyester resin, cobalt octoate (which acts as an accelerator), and methyl ethyl ketone peroxide^{22,23} (which acts as a catalyst) at 100 : 1 : 0.5 volume ratios, respectively.

Rheological measurements

Viscosity measurements were performed with a Bohlin Instruments cup and bob model Visco 88 Rheometer. At first, viscosities of the resin system were measured at different shear rate until the onset of gelation and it was found that the viscosities of the resin do not change appreciably over a large range of shear rate. Hence, the viscosity measurements were conducted using a constant shear rate of 60 s⁻¹ and constant temperature conditions 25, 40, 50, and 60°C. The viscosity as a function of time at constant shear rate was measured until the onset of resin gelation.

Cure kinetics measurements

The extent of reaction during the curing process was measured experimentally using a TA instruments DSC Q100 V 8.1 model operated under constant temperature conditions and the heat flow versus time was measured until the resin cure reaction was complete. To select suitable temperatures for the isothermal experiments, a dynamic DSC run at a heating rate 10°C min⁻¹ was first performed. Temperatures above but near the onset of reaction and below the peak heat flow were chosen for the constant temperature cure study.

CURE KINETICS MODELING

The task of the cure kinetics modeling is to uniquely define the curing reaction rate with its variables. The rate of reaction $d\alpha/dt$ is measured by the product of two functions namely, temperature dependant function $k(T)$ and cure conversion dependant function

$f(\alpha)$. The temperature dependant function, $k(T)$ is given by the Arrhenius form, as given in eq. (5).

$$k(T) = A \times \exp[-E/RT]. \quad (5)$$

The dependence of the reaction rate on the extent of reaction takes the form as given in eq. (6).

$$f(\alpha) = (1 - \alpha)^n. \quad (6)$$

DSC measures the amount of heat generated during curing reaction. The heat flow versus time was measured at the constant temperatures until the reaction was complete. The extent of cure reaction (or) the degree of cure at time t , $\alpha(t)$ can be determined from the measured DSC heat flow curves using eq. (7).

$$\alpha(t) = \Delta H_t / \Delta H_{tot}, \quad (7)$$

For a given isothermal temperature, ΔH_t is the accumulative heat of reaction up to curing time t and given by area under the heat flow curve at time t . ΔH_{tot} is the total enthalpy of the reaction and given by the total area under the heat flow curve. The steps involved in the modeling of cure kinetics are shown in Figure 1.

In this study, n th order cure kinetics model as given in eq. (8) was utilized to quantify the rate of degree of cure as a function of degree of cure and temperature.

$$d\alpha/dt = k(1 - \alpha)^n, \quad (8)$$

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

CURE VISCOSITY MODELING

The viscosity evolution of a reacting-resin system is mainly due to the structural changes imparted by the cross-linking cure reaction and the molecular mobility induced by the temperature variations. Hence, the chemical reaction induced viscosity modeling describes the change in viscosity as a function of the extent of cure reaction and the temperature as given in eq. (9).

$$\eta = f(\alpha, T) \quad (9)$$

where η is the viscosity in Pascal seconds, α is the extent of cure reaction (or) the degree of cure, T is the temperature in Kelvin.

The viscosity during resin curing can be determined by the combination of the data from the isothermal DSC analysis and isothermal rheological

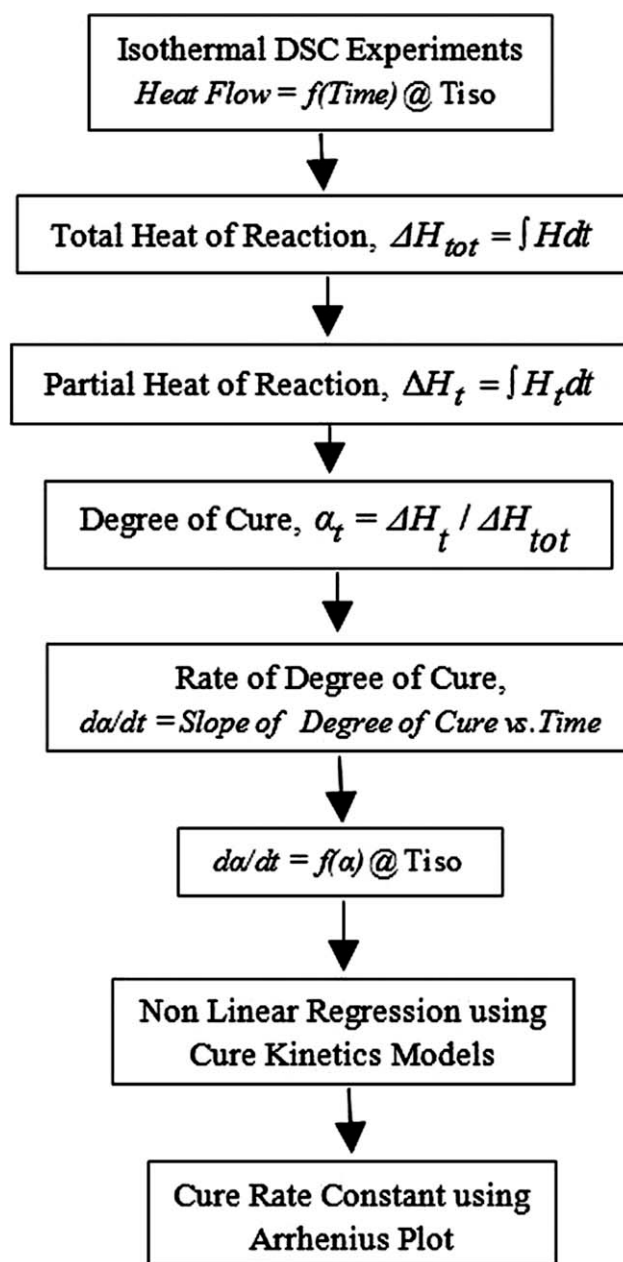


Figure 1 Cure kinetics modeling steps.

measurements. Once $\eta = f(t)$ and $\alpha = f(t)$ with constant cure temperature as a parameter are known, the viscosity can be modeled as a function of extent of cure reaction and the constant cure temperature, which is shown in Figure 2. In this study, the authors propose a regression model to quantify the viscosity change during curing reaction as a function of the degree of cure and the temperature.

RESULTS AND DISCUSSION

Constant temperature viscosity experiments

A series of constant temperature viscosity measurements at 25, 40, 50, and 60°C were conducted.

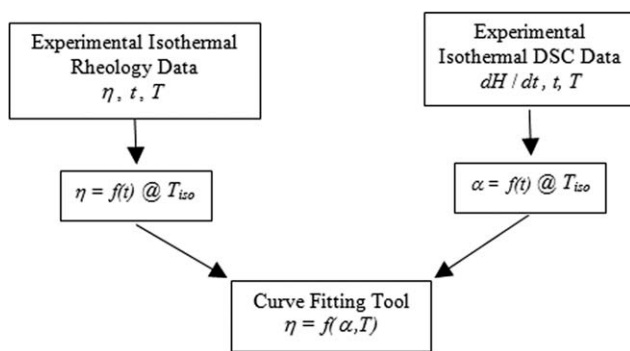


Figure 2 Viscosity modeling steps.

Figure 3 shows the monitored viscosity – time data over the range of applied constant temperatures.

From the Figure 3, it can be shown that the initial viscosity varies inversely with the applied cure temperature before the initiation of cure reaction causing the viscosity to be initially lower at higher temperatures, since the temperature makes the polymer chain move apart more rapidly than the cross-linking during this initial period. At the initial stages, the rise in temperature encourages the disentanglement before the sufficient cross-linking is obtained. Moreover, at the start of the experiment, there is a significant noise in the viscosity measurements largely because of the time taken for the resin temperature to reach the set point. It can also be seen that the evolution of viscosity increases with increasing polymerization reaction under constant temperature. Sufficient cross-linking does not occur until the onset of gelation (gel time) and viscosities almost remain constant until gelation starts. In RTM process; the industrial practices are to fill the mold within the 50% of the resin gelation time for the ease processing. In RTM process, the mold-fill time is longer (in the order of several minutes to hours) and

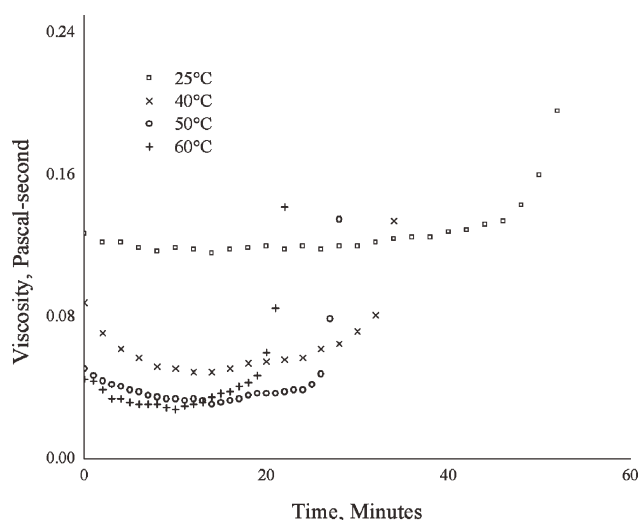


Figure 3 Viscosity as a function of time at different temperatures.

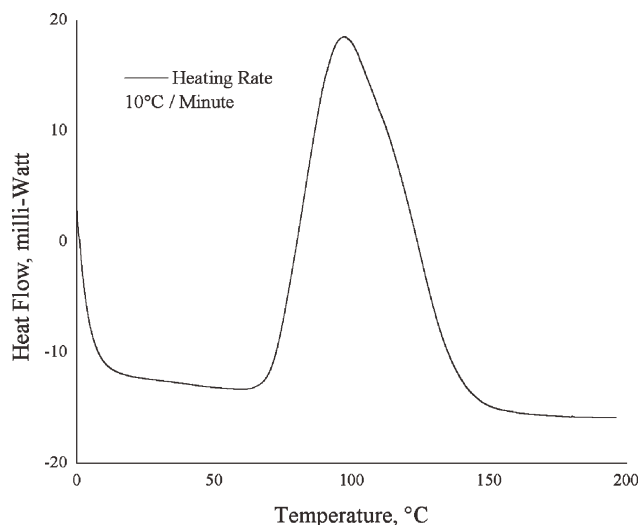


Figure 4 Dynamic heat flow curve of a medium reactive unsaturated polyester resin curing at different temperatures.

to satisfy the processing needs, the resin has longer gel time. The resins for such processes are tailored with the inhibitors to obtain the desired-gel time. From the DSC dynamic heat flow curve (Fig. 4), it was observed that the onset of gelation takes place around 70°C. Before the onset of gelation temperature, there expected no significant change in viscosity because of the slow exothermic reaction and hence viscosity remains constant during a large portion of time at the lower temperatures. This nature of the viscosity–time profile is also found in the published reports.^{4,5} Furthermore, the rate of change of viscosity increases with increasing temperature since this increases the cure rate. It may be mentioned that the onset of resin gelation occurs with the sudden rise in viscosity and the slope of viscosity–time curve increases with increasing applied temperatures, the time taken to reach the resin gelation decreases with the increase in applied cure temperatures, which is presented in Table I.

Differential scanning calorimetry experiments

Dynamic heating differential scanning calorimetry experiment

From Figure 4, it is evident that the onset of the curing reaction under these conditions is above 60°C

TABLE I
Time Rate of Viscosity at the Onset of Gelation at Different Temperatures

Temperature (°C)	Time rate of viscosity at the onset of gelation (Pa s min ⁻¹)
25	0.0034
40	0.0166
50	0.0204
60	0.0242

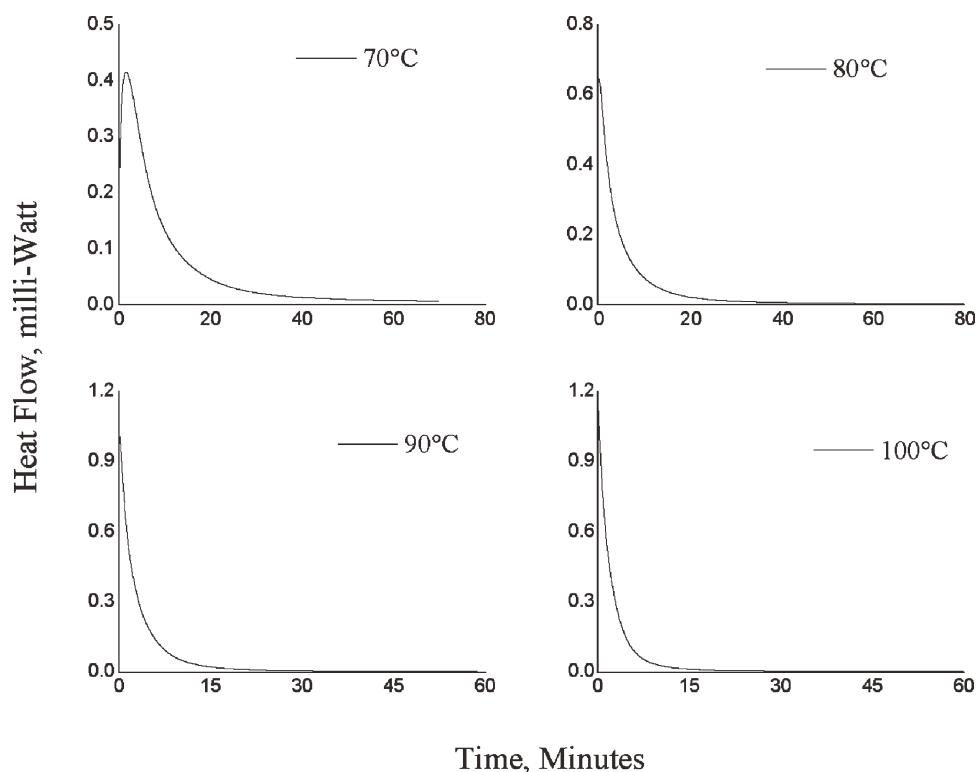


Figure 5 Isothermal heat flow of a medium reactivity unsaturated polyester resin curing at 70, 80, 90, and 100°C versus cure time.

and the maximum heat flow of curing reaction occurs around 105°C. The isothermal experimental temperatures were selected between the temperatures 60 and 105°C. The reason for selecting temperatures in this range is that below 60°C, the reaction is too slow and it will take an appreciable time for completion of the reaction, while above 105°C, the reaction is too fast and a significant part of the reaction is complete before the attainment of constant temperatures. Four temperatures of 70, 80, 90, and 100°C were chosen for conducting constant temperature curing experiments.

Constant temperature heating differential scanning calorimetry experiments

From Figures 4 and 5, it is evident that the heat flow rate is a function of temperature and time. With increasing cure temperature, the maximum heat flow rate increases and the time taken for reaction completion decreases.

Rate of degree of cure as a function of degree of cure and temperature

The constant temperature heat flow versus time data as given in Figure 5 was numerically integrated to obtain the degree of cure using eq. (6), which is shown in Figure 6. From the same figure, it may be

mentioned 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 the degree of cure.

As can be seen in Figure 7, at a given temperature, the rate of degree of cure increases with the degree of cure and attains a maximum at $\alpha < 0.1$, then gradually decreases and finally tends to 0. It has been shown that for a given conversion, higher the temperature, higher the rate of degree of cure. Moreover, Figure 7 illustrates the comparison of variation of rate of degree of cure with degree of cure between n th order kinetics model and experimental data. It can be observed that the experiments exhibit its maximum rate of degree of cure at the earlier stages of cure reaction. To further illustrate, the rate of degree of cure predicted by the n th order kinetics model is closer to the experimental data at all constant temperatures. It may be mentioned that the model parameters in n th order kinetics model have been evaluated using nonlinear-regression analysis to our experimental data; the values of the parameters for the n th order kinetics model as well as the correlation factors for the fits are presented in Table II. In addition, the n th order kinetics model has been forced with the average kinetic parameter n and the values of the rate constants are presented in Table III.

The temperature dependence of the kinetic rate constants of the n th order kinetics model (as given

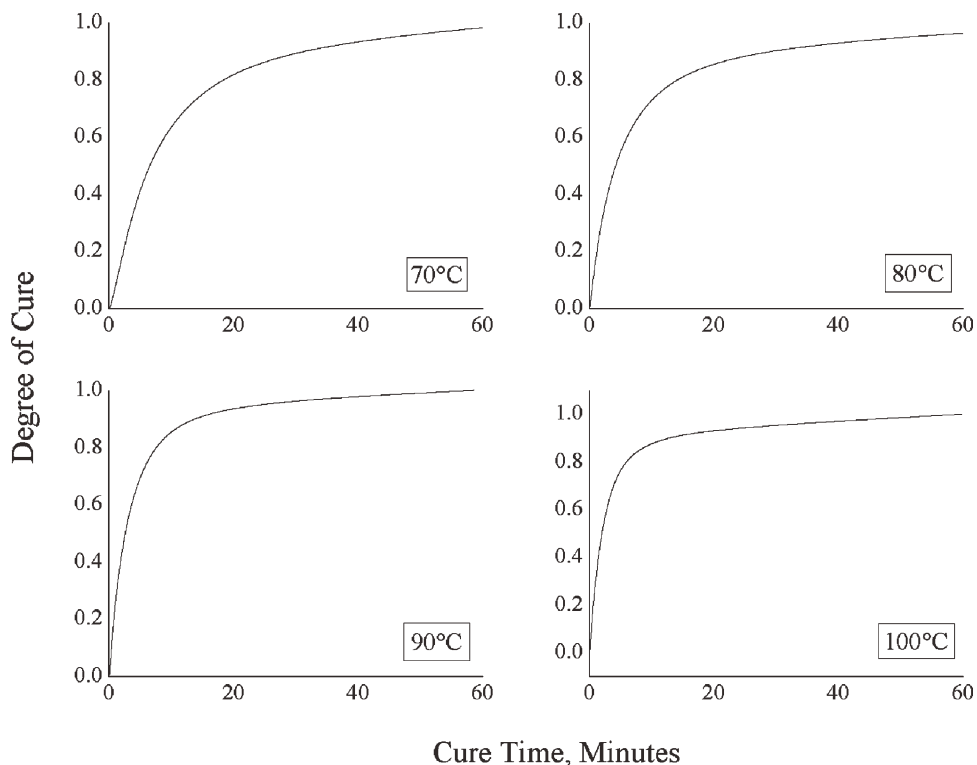


Figure 6 Degree of cure of a medium reactive unsaturated polyester resin curing at 70, 80, 90, and 100°C versus cure time.

in Table III) has been determined by fitting to the Arrhenius form as shown in Figure 8. The best fit of Arrhenius form relating rate constants and tempera-

ture is given by eq. (10) and the frequency factor (A) and activation energy (E) have been obtained as $2.7 \times 10^5 \text{ min}^{-1}$ and $41.43 \text{ kJ mol}^{-1}$, respectively.

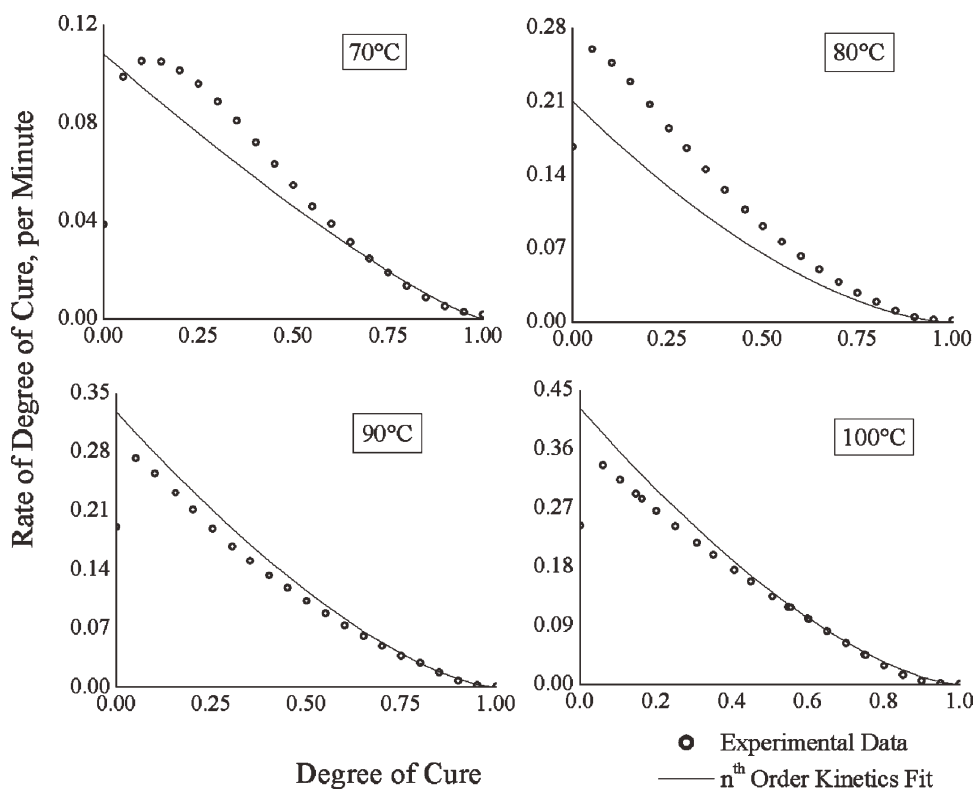


Figure 7 Comparison of experimentally obtained rate of degree of cure versus degree of cure at 70, 80, 90, and 100°C with that predicted by the n^{th} order kinetics model.

TABLE II
Parameter Values for the n th Order Kinetics Model
Obtained by Fitting to the Experimental Data

Isothermal temperature (°C)	Empirical rate constant K, (min ⁻¹)	Kinetic parameter (n)	Goodness of fit (R^2)
70	0.108	1.230	0.963
80	0.210	1.686	0.997
90	0.327	1.513	0.997
100	0.422	1.552	0.992

The rate equation defining the rate of degree of cure as a function of degree of cure and temperature is given in eq. (11):

$$\ln(k) = (-4982/T) + 12.508, \quad R^2 = 0.962 \quad (10)$$

$$d\alpha/dt = 2.7 \times 10^5 \times \exp(-4982/T) \times (1 - \alpha)^{1.495} \quad (11)$$

Determination of degree of cure at different isothermal temperatures

The degree of cure as a function of time at different isothermal temperatures was obtained by integrating the rate equation given by eq. (11) with the limits, at time $t = 0$, degree of cure $\alpha = 0$. The obtained equation relating to degree of cure as a function of time at any isothermal temperature is given in eq. (12) and the obtained degree of cure as function of time curves at 25, 40, 50, and 60°C are given in Figure 9.

$$\alpha = [(1.3 \times 10^5) \times \exp(-4982/T) \times t]^{0.495} \quad (12)$$

Superimposed degree of cure versus viscosity versus cure time curves

With cure time as the parameter, cure viscosity and degree of cure can be plotted for the temperatures 25, 40, 50, and 60°C, which is shown in Figure 10. It shows the parallel advancement of viscosity and degree of cure up to resin gelation for the applied isothermal temperatures 25, 40, 50, and 60°C. It has been shown that the time for resin gelation decreases with the increase in temperature. As can be seen from the

TABLE III
Parameter Values for the n th Order Kinetics Model
Obtained by Forcing Average Reaction Order

Isothermal temperature (°C)	Empirical rate constant K, (min ⁻¹)	Kinetic parameter (n)	Goodness of fit (R^2)
70	0.1189	1.495	0.938
80	0.1922	1.495	0.975
90	0.3227	1.495	0.985
100	0.4081	1.495	0.976

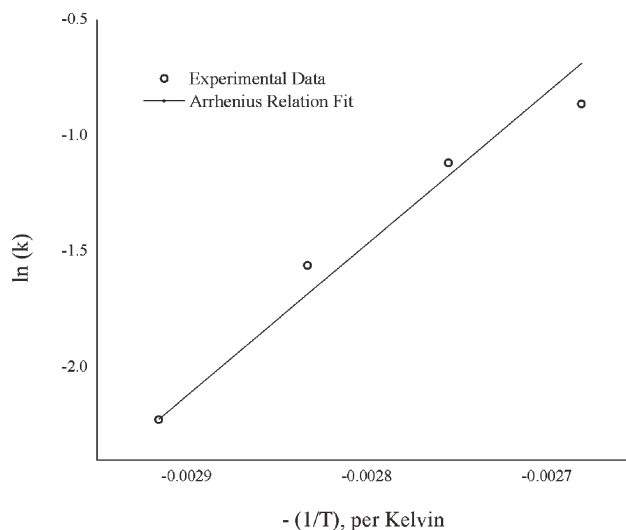


Figure 8 Temperature dependence of the cure kinetics rate constants.

same figure, the onset of resin gelation occurs at the more or less equal degrees of cure ($\alpha_{\text{gel onset}} = 0.6 - 0.65$). The time interval between complete gelation and onset decreases with increased applied temperature. Moreover, the degree of cure at the peak gelation increases with increasing temperature. The reason for this could be because of the increased reaction as a cause of increased local motion of the chain segment triggered by increase in the curing temperature.^{1,7}

Viscosity as a function of degree of cure and temperature

Before trying the present model, the experimental viscosity data was tried with various available models in the published reports, which were found

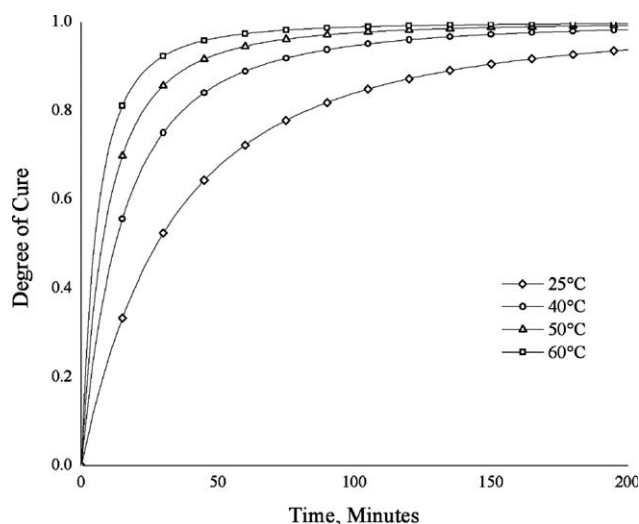


Figure 9 Degree of cure as a function of cure time at 25, 40, 50, and 60°C.

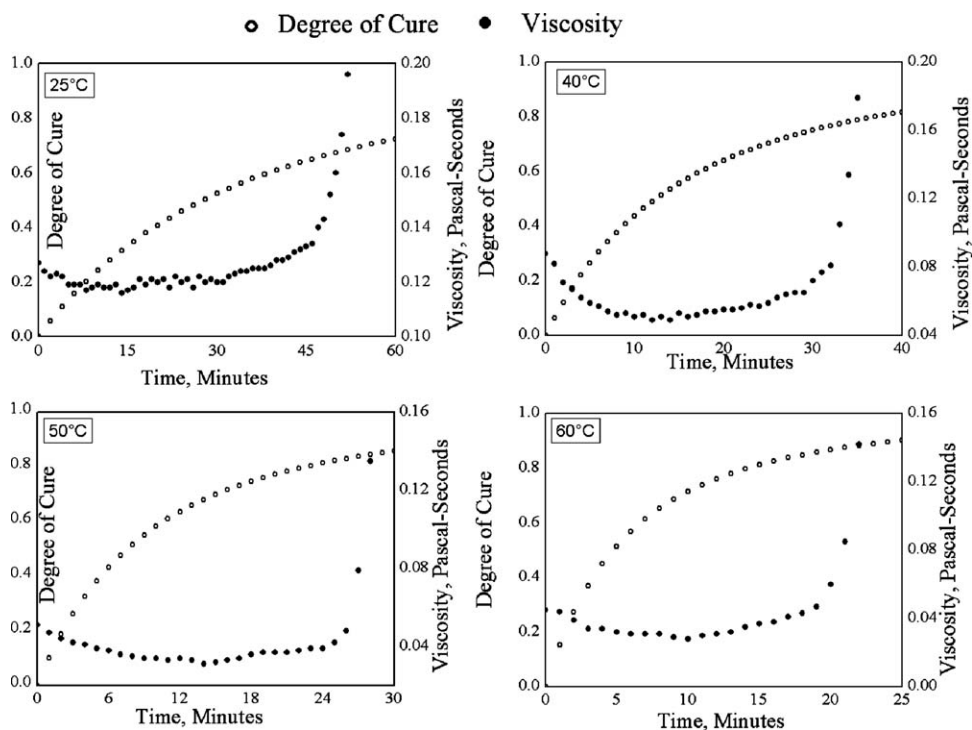


Figure 10 Degree of cure versus viscosity versus cure time for temperatures 25, 40, 50, and 60°C.

TABLE IV
Viscosity Data Fit to Literature Models

Model	Equation	Parameter	Correlation coefficient (R^2)
Henne ¹	$\eta(T^1, \alpha) = \eta_{\text{V}} \times \exp [(T_{\text{rheo}}/T^1) + B\alpha]$	$\eta_{\text{V}} = 3.82 \times 10^{-6}$ Pas $T_{\text{rheo}} = 3098$ K $B = -0.271$	0.92
Dusi ³	$T^1 \eta(T, \alpha) = \eta_0 \times \exp[(E_{\eta}/RT) + B\alpha^2]$	$\eta_0 = 2.83 \times 10^{-6}$ Pas $E_{\eta}/R = 3176$ K $B = -0.304$	0.931
Shanku ⁷	$\eta(T, \alpha) = \eta_0 \times \exp[(E_{\eta}/RT) + A\alpha + B\alpha^2]$	$\eta_0 = 2.18 \times 10^{-6}$ Pas $E_{\eta}/R = 3266$ K $A = -0.269$ $B = 4.4 \times 10^{-2}$	0.936

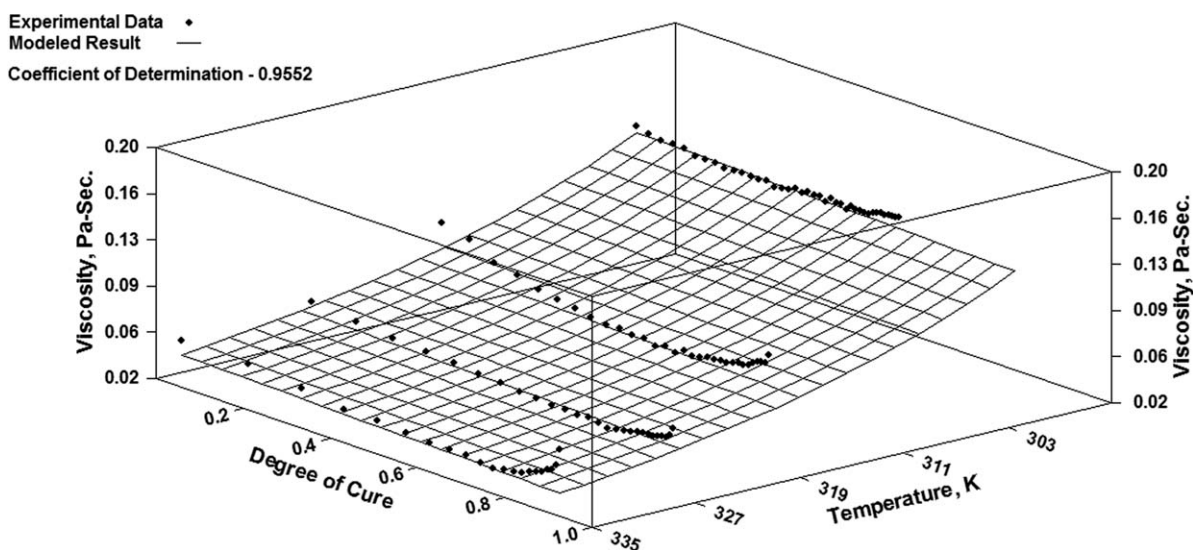


Figure 11 Viscosity during resin cure as a function of degree of cure and temperature.

unsuitable because of the lower degree of correlation coefficient. The results of the viscosity data fit to the available models are tabulated in Table IV. A nonlinear-regression analysis of viscosity advancement data correlating degree of cure and temperature was performed and a comparison of actual and modeled results is given in Figure 11. The empirical form given in eq. (13) gives a better definition with a goodness of fit 0.96 in relating viscosity evolution up to resin gelation to the extent of cure chemical reaction and the temperature profile applied to cure the resin.

$$\eta(T, \alpha) = 5.846 \times 10^{-7} \times \exp(3649/T) - (8.33 \times 10^{-3} \times \alpha), \quad \alpha < \alpha_{\text{gel}} \quad (13)$$

where η is the viscosity in Pascal seconds, T is the temperature in Kelvin, and α is the degree of cure.

Less number of modeling parameters is preferred to model the physics mathematically. In the published reports, Henne and Shanku are four parameter models in comparison to the three parameter model, which is newly proposed for the rheokinetics. All the compared published reports predicts an exponential variation of viscosity with the degree of cure and falls short to predict the linear variation of viscosity with the degree of cure, which depends on the nature of the resin. Hence, the proposed model is preferred over the published reports irrespective of its closeness to data fit for the medium reactive unsaturated polyester resins.

The developed three parameter empirical model exhibit two regions namely temperature dependant and cure reaction dependant. From the eq. (13), it can be seen that the viscosity varies exponentially with the applied temperature and linearly with the extension of cure reaction. It may be mentioned that the form describing temperature dependence of viscosity resembles the Arrhenius form. The parameter value 5.846×10^{-7} pas resembles the zero-time viscosity (η_0) and the value 3649 °K resembles the energy barrier to flowing E_η/R in the Arrhenius form. E_η can be correlated to the structural changes during resin cure and it needs to be overcome in order for the motion of polymer chains to make the resin flow. At higher E_η , the harder is the movement of polymer chains, which might be due to the cure reaction resulting in the entanglement and strong interactions of the cross-linking polymer chains.

CONCLUSION

A correlation for viscosity during curing of medium reactive unsaturated polyester resin as a function of temperature and degree of cure has been developed.

From the rheological experiments, it has been observed that the viscosity was a function of temperature and the degree of cure reaction. The viscosity evolution during resin cure can be attributed to the structural changes caused by the rapid cross-linking reaction caused by applied cure temperature. It has been found that the viscosity decreases initially with increase in temperature at the lower degree of cures and viscosity starts increasing after attaining a substantial amount of cure reaction. An empirical regression model has been proposed for the advancement of viscosity during resin curing up to the onset of gelation. The proposed model explicitly depends on the extent of the cure reaction and the applied isothermal temperature. Good agreement is seen between predicted and measured experimental viscosity during cure for the range of temperature studied.

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