

A Comparison of Chemorheological Models for Thermoset Cure

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Synopsis

A chemorheological study of a thermoset system consisting of diglycidyl ether of bisphenol-A (DGEBA) epoxy resin and a mixture of two aromatic amine curing agents; 4,4'-methylenedianiline (MDA) and *m*-phenylene diamine (*m*-PDA), was conducted. Experimentally obtained viscosity data were checked against the predictions of two different viscosity models; one based on a phenomenological equation obtained by modification of the classical Williams-Landel-Ferry (WLF) equation and the other based on an extension of the branching theory originally proposed by Flory. In general, the predictions of both models were in excellent agreement with experimentally obtained isothermal and dynamic viscosity data. The branching theory model was found to have a slight advantage over the phenomenological equation model in describing the viscosity prior to gelation in a fast heating cure cycle.

INTRODUCTION

Modeling of chemorheology of thermosetting polymers has recently generated considerable interest among polymer scientists and engineers, due primarily to the ever-increasing use of thermosets as the matrix material in advanced composites.^{1,2} The chemorheological behavior of the matrix resin is affected by the structural changes caused by cure reactions (cure kinetics) and by the variations in molecular mobility (rheology) induced by changes in temperature. The chemorheology of the matrix resin determines the extent of reaction and the volume fraction of the matrix and thus the physical/mechanical properties of cured composites.

To establish a chemorheological model for thermoset cure, one must evaluate the change of viscosity as a function of the applied cure cycle and the cure kinetics of the resin formulation. Early efforts to predict the chemoviscosity of thermosets were essentially based on fits of measured viscosity to an exponential function of time, which included empirical reaction rate parameters.³⁻⁹ Various modifications were later made to these models by introducing additional parameters while retaining the general form of the viscosity dependence,^{2,10} but these models remain empirical in nature and are not readily related to the chemistry and the physical properties of the curing system.

A more fundamental approach was taken by others who modeled the network growth, and hence the increase in viscosity, in terms of the change of the weight-average molecular weight during cure.¹¹⁻¹³ The precursor for those works was the classical study by Flory of molecular weight distribution in

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nonlinear polymers which led to the development of the branching theory.¹⁴ The branching theory was later expanded by Stockmayer¹¹ to describe the growth of a three-dimensional network as a function of polymer concentration, type, and fractionality. Using a simplified form of Stockmayer's molecular weight equation, Lipshitz and Macosko¹³ have developed the following equation relating viscosity to the molecular weight:

$$\ln n = \ln A + S \ln \left(\frac{\overline{MW}}{MW_0} \right) + \frac{D + C \ln \left(\frac{\overline{MW}}{MW_0} \right)}{RT} \quad (1)$$

where A , S , D , and C are obtained by best fit. This equation is useful in describing viscosity during cure of thermosets up to the gel point, and has been utilized recently by Schmitt et al.¹⁵ and Bidstrup and Macosko.¹⁶

In recent years, several researchers have invoked the concept of free volume to calculate and predict the changes in thermoset viscosity during cure.¹⁷⁻²¹ Common to all those studies is the use of various modified forms of the classical Williams-Landel-Ferry (WLF) equation.²² A modification of the WLF equation is necessary since the glass transition of the curing resin is a function of extent of reaction, and thus it varies during the "in situ" polymerization.

The prerequisite for the application of both the branching theory and the modified WLF equation to thermosets is the derivation of an accurate kinetic model. From such a model, the correlations between extent of reaction and molecular weight (branching theory), and extent of reaction and glass transition temperature (modified WLF equation) can be established and viscosity predictions can be made.

In this study, the branching theory and the free volume concept were both used to predict viscosity during isothermal and nonisothermal cure and a comparison between these two approaches was made. The main objectives of this research were: (1) to develop chemorheological models for the formulation used herein and (2) to compare the viscosity predictions from the branching theory and a modified form of the WLF equation.

EXPERIMENTAL

Materials

As a continuation of our comprehensive program in the area of composites, we are currently exploring the possibility of production of filament-wound composite structures beginning with the preimpregnated tape (prepreg). For that purpose, a resin formulation composed of a bifunctional epoxy resin of the DGEBA type and a mixture of two aromatic amines, methylene dianiline (MDA) and *m*-phenylene diamine (*m*-PDA), was investigated. This and similar formulations^{19, 21, 23, 24} have generated considerable interest as candidates for the matrix material for filament wound structures. To simulate the actual situation whereby filament winding starts from the prepreg, a series of experiments in this study advanced the neat resin to the same extent of cure as in the prepreg.

The epoxy resin used in this study was of the diglycidyl ether of bisphenol-A (DGEBA) type (Shell's Epon 826), containing a small amount of higher oligomeric fractions (87.6% of $n = 0$; 7.4% of $n = 1$; 1.0% of $n = 2$; and 4% of dihydroxy species).²⁵ A 60/40 mixture, by weight, of 4,4'-methylenedianiline (MDA) and *m*-phenylene diamine (*m*-PDA), both of which were obtained from Aldrich Chemical Company, was used to cure the resin. The stoichiometric ratio of DGEBA : MDA : *m*-PDA was 100 : 12.6 : 8.4, corresponding to an amine-to-epoxy ratio of 1.0. The production of prepreg using this formulation was investigated by Claps,²⁶ who found that the formulation must first be advanced, that is, partially cured, to successfully process the prepreg. According to Claps, the formulation must be cured to approximately 20–25% conversion. The preparation of the advanced resin begins by heating the epoxy resin to 100°C in a separate container. Simultaneously, the mixture of curing agents was heated to 80°C to form a liquid and then added to the hot epoxy. The system was maintained at 100°C for 5 minutes, followed by cooling to 40°C at a rate of 10°C/min. The samples were then poured into vials and quenched into dry ice where they were kept no longer than 48 h. The freshly mixed resin was prepared by heating the curing agent mixture until a liquid formed and then adding it to the epoxy at room temperature. The samples are then used immediately or stored in individual containers in dry ice.

Viscosity Measurements

The viscosity of the freshly mixed and the advanced cure resin was determined by a Brookfield Digital Viscometer, model HATDV-II. The temperature of the systems was maintained and controlled by a Brookfield Thermosel and an Omega Programable Temperature controller. A SCA-21 spindle was used at a steady shear rate of 5.60 s⁻¹. The resin was prepared for the viscosity measurement according to the following procedure: First, the sample was preheated to 40°C and maintained at that temperature for about 5 min until a constant viscosity reading was obtained. The sample was then ramped at 10°C/min until it reached the preset isothermal hold temperature. This heating schedule minimized the temperature overshoot and provided excellent reproducibility of the results. The freshly mixed resin was prepared for viscosity measurement according to the following procedure: the test chamber was preheated to the isothermal hold temperature and then the resin was added to the test chamber and the viscometer started. Data acquisition was started exactly one minute later. During this time, no further reactions took place. Isothermal runs were performed at 60, 70, 80, 90, 100, and 110°C, and the reproducibility was better than 5%. A series of nonisothermal runs simulating different cure cycles were performed at different heating rates. All nonisothermal runs' temperature profiles are superimposed on the corresponding figures throughout the text.

Differential Scanning Calorimetry

A Du Pont 1090 Thermal Analyzer connected to a 910 DSC module was used to measure the heat flow as a function of time after calibration with high purity Indium (Du Pont thermometric standard). Kinetic data as well as the

TABLE I
Kinetic Parameters for the Formulation Used in This Study

$k_1 = 8.64 \times 10^6 \exp(-6.55 \times 10^4/RT)$
$E_{a1} = 15.7 \text{ kcal/mol}$
$k_2 = 1.25 \times 10^6 \exp(-4.32 \times 10^4/RT)$
$E_{a2} = 10.3 \text{ kcal/mol}$
$m = 1.68 - 2.042 \times 10^{-3}T$

relationship between the glass transition and cure kinetics were generated according to the procedure described in detail elsewhere.²⁷

RESULTS AND DISCUSSION

Cure Kinetics

In our previous communications we reported a detailed description of how the cure kinetics of this and similar formulations were evaluated^{24,27} and will present only a brief summary here. An autocatalytic kinetic model of the following form:

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

was found to fit the data very well. The expressions obtained for kinetic parameters k_1 , k_2 , E , and m compared well with those reported in the literature²⁵ and are presented in Table I. The resulting kinetic expressions were then used in conjunction with Eq. (2) and solved using a fourth-order Runge-Kutta method of integration²⁸ for a given time-temperature profile. Figure 1 shows the extent of reaction versus time plot for several isothermal temperatures.

A correlation between the extent of reaction and the corresponding glass transition temperature was obtained from DSC scans of partially cured samples. A log plot of glass transition as a function of extent of reaction is shown in Figure 2. The observed dependence of T_g on extent of reaction can be approximated by the following exponential equations:

$$T_g = 256.4 \exp(1.590 \cdot 10^{-3}\alpha) \quad \text{for } \alpha < 24\% \quad (3a)$$

$$T_g = 233.2 \exp(5.628 \cdot 10^{-3}\alpha) \quad \text{for } \alpha \geq 24\% \quad (3b)$$

Qualitatively, similar temperature dependence of the extent of reaction was reported by Cizmecioglu and co-workers, who studied cure of a tetrafunctional epoxy formulation.²⁹

The above described kinetic information was then used in conjunction with two methods for the prediction of viscosity during cure, based upon the modified WLF equation and the branching theory.

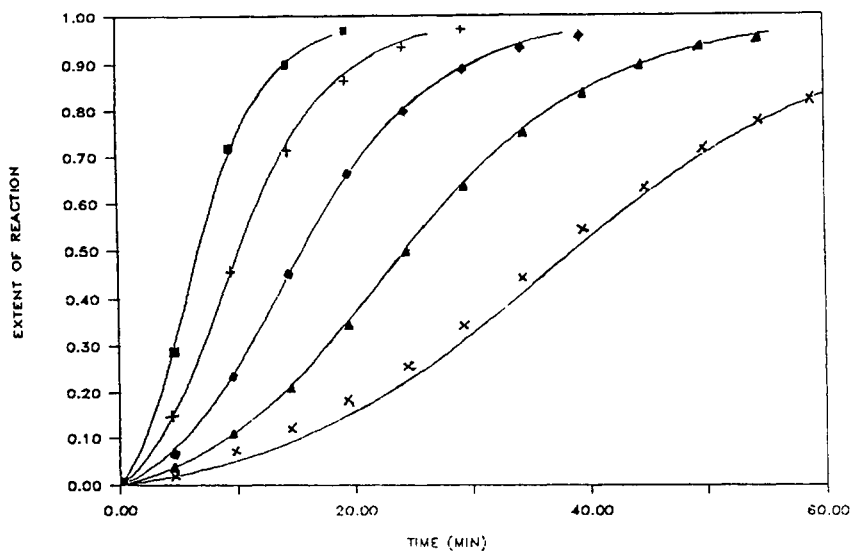


Fig. 1. Extent of reaction as a function of cure time at several isothermal temperatures ($- \times - 90^{\circ}\text{C}$, $- \blacktriangle - 100^{\circ}\text{C}$, $- \blacklozenge - 110^{\circ}\text{C}$, $- + - 120^{\circ}\text{C}$, $- \blacksquare - 130^{\circ}\text{C}$).

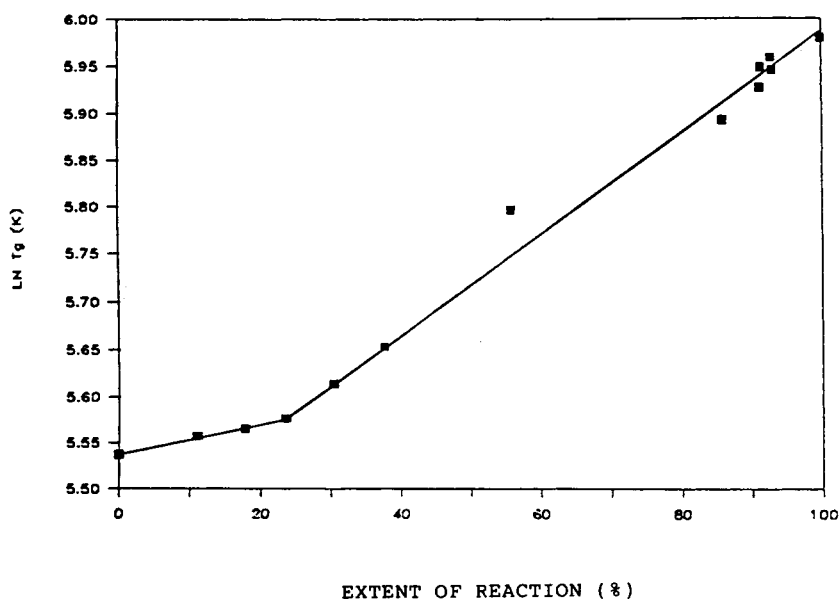


Fig. 2. Glass transition temperature as a function of extent of reaction.

Viscosity Predictions by a Phenomenological Equation

Unlike thermoplastic polymers, for which the WLF equation was derived, thermosets undergo chemical reactions during cure, resulting in a continuous change of polymer structure and a simultaneous increase in the glass transition temperature. The rate of network formation is based on the kinetics of cure, which, in turn, is a function of temperature. The parameters C_1 and C_2

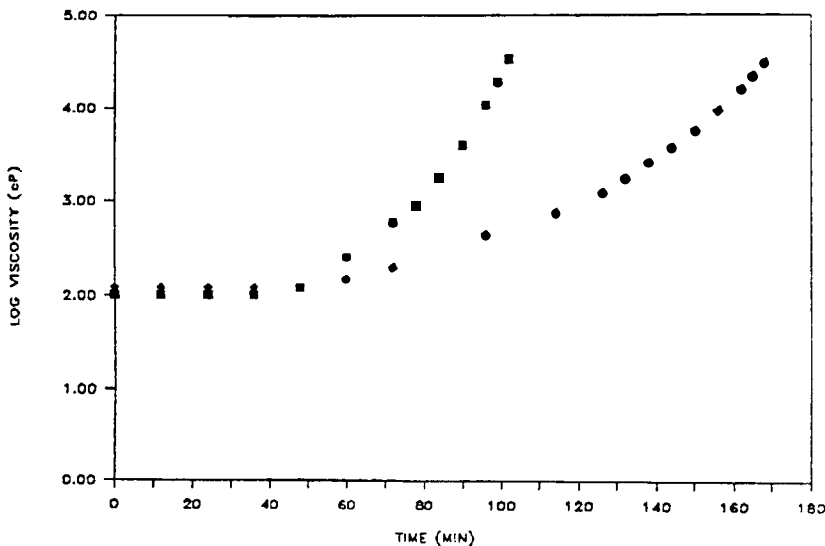


Fig. 3. Viscosity as a function of cure time (—◆— 60°C, —■— 70°C).

could also vary with time and cure temperature and hence to predict thermoset viscosity one must incorporate the following correlations into the classical WLF equation:

$$\alpha = f(T, t) \quad (4)$$

$$T_g = g(\alpha) \quad (5)$$

$$C_1 = h(T) \quad (6)$$

$$C_2 = i(T) \quad (7)$$

where α is the extent of reaction, T_g the glass transition temperature, and C_1 and C_2 parameters. The resulting phenomenological equation which was utilized in this study is of the following general form:

$$\log \frac{\eta}{\eta_g} = \frac{-C_1(T)[T - T_g(T, t)]}{C_2(T) + T - T_g(T, t)} \quad (8)$$

where η_g was assumed to remain constant. Equations (4) and (5) have been obtained from our kinetic analysis as described in the cure kinetics section. To obtain Eqs. (6) and (7), a series of viscosity measurements were performed, the results of which are shown in Figures 3 and 4. From these data, Eqs. (6) and (7) were evaluated by rearranging Eq. (8) as described elsewhere,²⁷ so that the parameters C_1 and C_2 can be determined from the slope and intercept. The

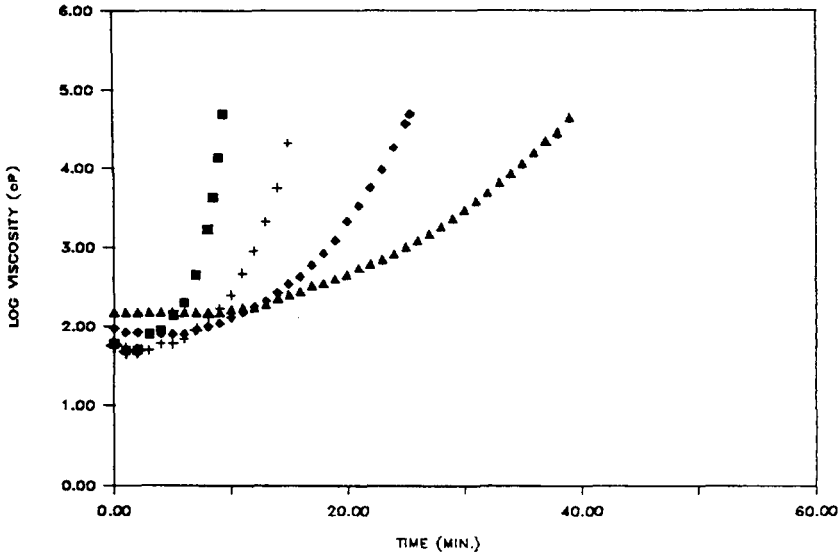


Fig. 4. Viscosity as a function of cure time (-▲- 80°C, -◆- 90°C, -+- 100°C, -■- 110°C).

parameters C_1 and C_2 were found to exhibit the following form:

$$C_1 = 1.66 \cdot 10^3 \cdot \exp(-1.65 \cdot 10^3/T) \quad T > 351 \text{ K} \quad (9a)$$

$$C_1 = 15.03 \quad T \leq 351 \text{ K}$$

$$C_2 = 1.18 \cdot 10^8 \cdot \exp(-5.30 \cdot 10^3/T) \quad T > 351 \text{ K} \quad (9b)$$

$$C_2 = 33.57 \text{ K} \quad T \leq 351 \text{ K}$$

where T is in degrees Kelvin. Upon substitution of Eqs. (4)–(7) into Eq. (8), viscosity predictions can be made.

Viscosity Prediction by the Branching Theory

Stockmayer¹¹ expanded Flory's original work by deriving a molecular weight expression as a function of degree of cure which Macosko and Miller³⁰ later simplified into the following form:

$$\overline{MW}(P_e) = \frac{P_e m_{a'} + P_a m_{e'}}{P_e m_a + P_a m_e} + \frac{P_a P_e [P_e (f_a - 1) M_e^2 + P_e (f_e - 1) M_a^2 + 2 M_a M_e]}{(P_e m_a + P_a m_e) [1 - P_a P_e (f_a - 1)(f_e - 1)]} \quad (10)$$

$$m_a = \frac{\sum_i M_A f_i A_i}{\sum_i f_i A_i} \quad \text{and} \quad m_{a'} = \frac{\sum_i M_A^2 f_i A_i}{\sum_i f_i A_i} \quad (11)$$

$$m_e = \frac{\sum_i M_E f_i E_i}{\sum_i f_i E_i} \quad \text{and} \quad m_{e'} = \frac{\sum_i M_E^2 f_i E_i}{\sum_i f_i E_i} \quad (12)$$

where M_e is the average epoxy molecular weight, M_A the average amine molecular weight, i the total number of species, A_i the moles of amine i , and E_i the moles of epoxy i . The formulae for M_a , M_e , M_a' , M_e' were designed to account for the possible existence of more than one species of amine or epoxy, assuming that each species has its own molar concentration and functionality. In this study, M_e was taken as 368 g/mol and M_a as 153 g/mol. The equation can further be simplified by relating the extent of reaction of the amine, P_a , to the extent of reaction of the epoxy, P_e , using:

$$P_a = \frac{f_e}{rf_a} P_e \quad (13)$$

where r is the amine to epoxy ratio which in this case is equal to 1.0. The extent of reaction of the epoxy, P_e , was taken to be equal to α derived from our kinetic analysis. The final form of equation 10 is:

$$\frac{\overline{MW}}{MW_0} = 1 + \frac{1.52 + 5.80P_e^2}{1 - 3P_e^2} \quad (14)$$

where \overline{MW} is the average molecular weight and MW_0 is the molecular weight at zero conversion which was calculated to be 333.3 g/mol. The next step uses Eq. (1) and the previously obtained viscosity data, by which we proceeded to evaluate the parameters of that equation by rearranging it into the following

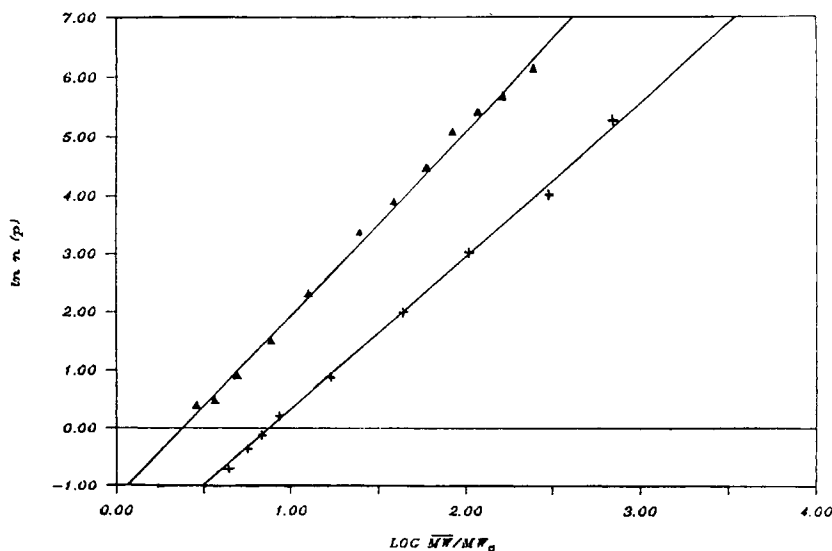


Fig. 5. \ln viscosity versus $\ln MW/MW_0$ as a function of cure temperature ($-\triangle-$ 80°C, $-+-$ 100°C).

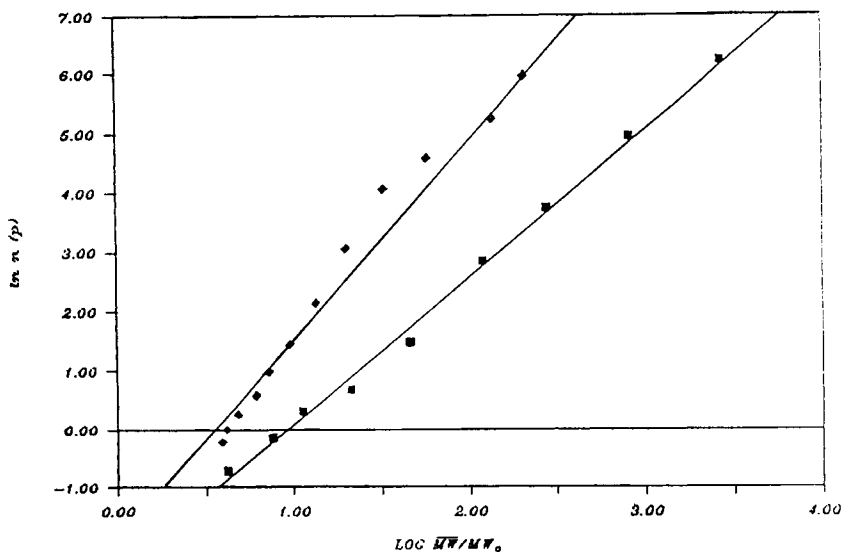


Fig. 6. $\ln n$ versus $\ln \overline{MW}/MW_0$ as a function of cure temperature (\blacklozenge - 90°C , \blacksquare - 110°C).

form:

$$\ln n = \ln A + \frac{D}{RT} + \left[S + \frac{C}{RT} \right] \ln \frac{\overline{MW}}{MW_0} \quad (15)$$

When log viscosity is plotted versus $\log \overline{MW}/MW_0$, we get $(S + C/RT)$ as the slope and $(\ln A + D/RT)$ as the intercept, as shown in Figures 5 and 6. When the individual values of the slope are plotted versus the corresponding $1/T$, the new intercept is equal to S and the new slope is equal to C/R . The same technique can be used on the intercept $(\ln A + D/RT)$ to yield the constants A and D/R . The resulting constants for Eq. (1), evaluated in the temperature range from 80° – 110°C , are presented in Table II. These values were then substituted back into Eq. (1) from which the viscosity was calculated.

Comparison of the Models: Isothermal and Dynamic Cases

Let us now show examples of comparisons between the predicted and the experimentally obtained viscosity. The first set of four figures (Figs. 7–10) the experimental isothermal viscosity data with the predictions of phenomenologi-

TABLE II
Constants for Equation (1)

$A = 2.07 \times 10^7 \text{ NS/M}^2$
$S = 5.12 \text{ NS/M}^2$
$D/R = 4.94 \times 10^3 \text{ J/gmol K}$
$C/R = 2.90 \times 10^3 \text{ J/gmol K}$
$80^\circ\text{C} \leq T \leq 110^\circ\text{C}$

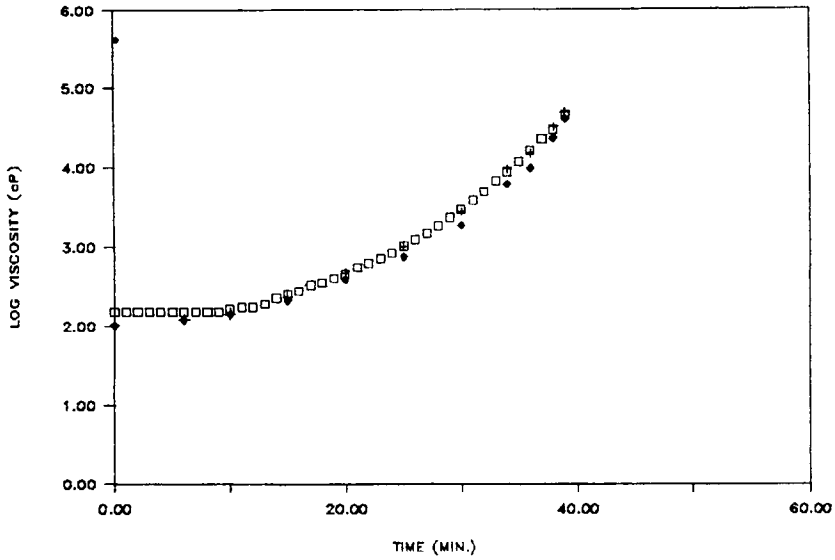


Fig. 7. Viscosity as a function of cure time. Comparison of experimental and predicted results at 80°C (\square - exp, + - PHEN, \blacklozenge - MW).

cal (PHEN) and branching theory models. One reason for a slight discrepancy observed at low viscosities is that the Brookfield Viscometer has a limited sensitivity at lower viscosities (5% of maximum or 25 Poise), and hence experimental errors could occur. In addition, there are possibly inherent sources of error in each model. The phenomenological model shows some deviation from experimental data early into the run, although the agreement

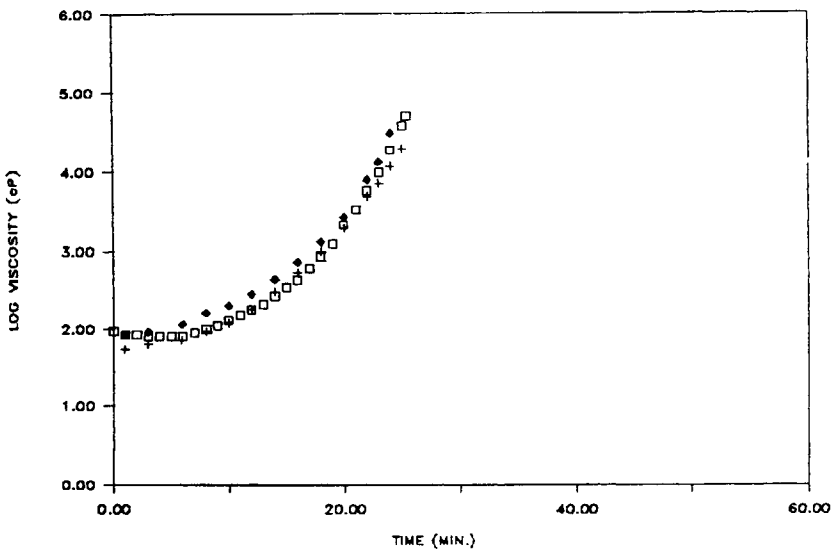


Fig. 8. Viscosity as a function of cure time. Comparison of experimental and predicted results at 90°C (\square - exp, + - PHEN, \blacklozenge - MW).

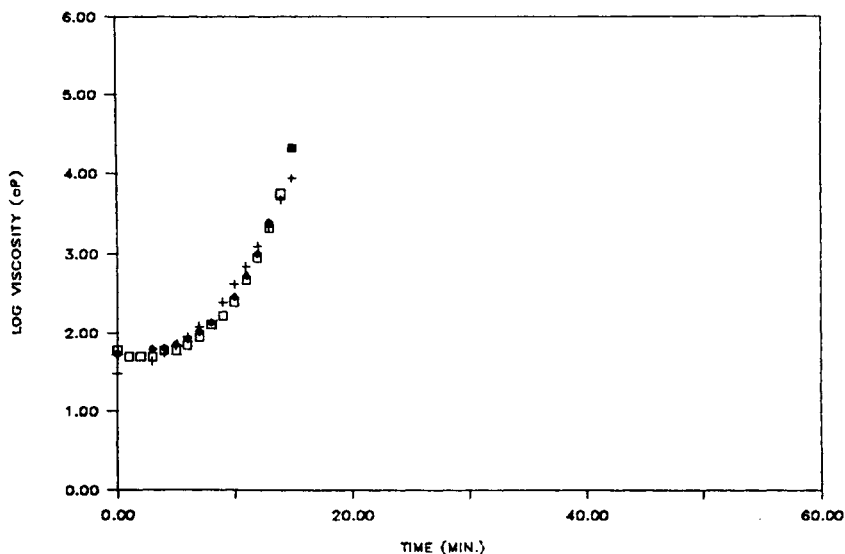


Fig. 9. Viscosity as a function of cure time. Comparison of experimental and predicted results at 100°C (\square - exp, + - PHEN, \blacklozenge - MW).

between the predicted viscosity and the experimental data improves as the polymer cure continues.

Branching theory showed excellent agreement with experimental data, especially at high temperature. Slight deviation observed at lower temperature may be due to the observed nonlinearity at very low viscosity, as seen in Figures 5 and 6. But, in general, both models showed excellent agreement between experimental and predicted results for isothermal viscosity, which is

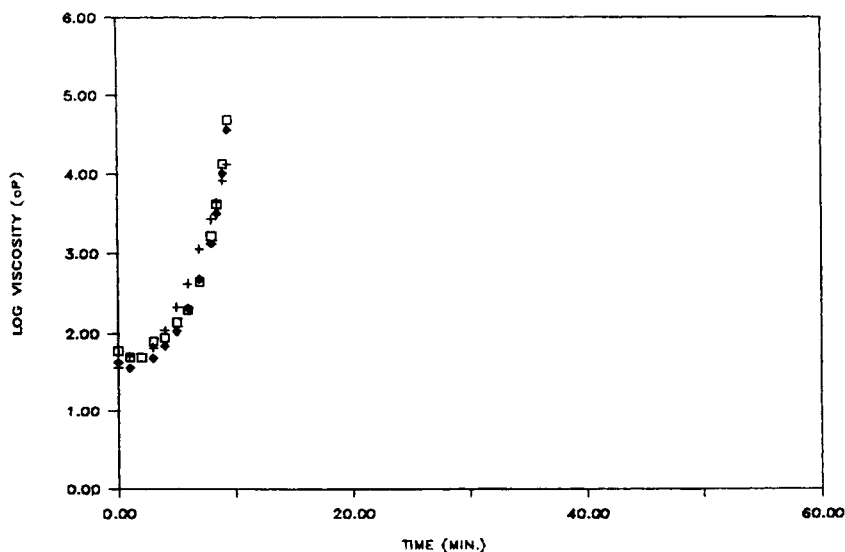


Fig. 10. Viscosity as a function of cure time. Comparison of experimental and predicted results at 110°C (\square - exp, + - PHEN, \blacklozenge - MW).

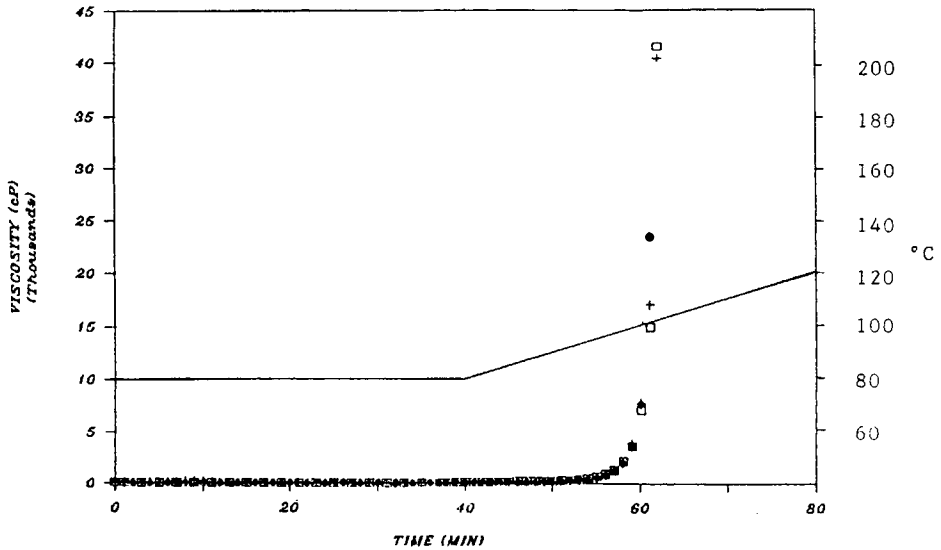


Fig. 11. Viscosity as a function of cure time. Comparison of experimental and predicted results of a simulated isothermal and dynamic cure cycle at $1^{\circ}\text{C}/\text{min}$ (\square - exp, $+$ - PHEN, \blacklozenge - MW).

particularly clear when one considers that the maximum discrepancy was less than 100 centipoise. We now turn our attention to the comparison of predicted versus experimental viscosity for a series of cure cycles in which an isothermal stage was followed by a dynamic stage. Figures 11–13 present the viscosity profiles for the freshly mixed formulation obtained by isothermally curing the system for 40 minutes at 80°C , and then ramping the system at

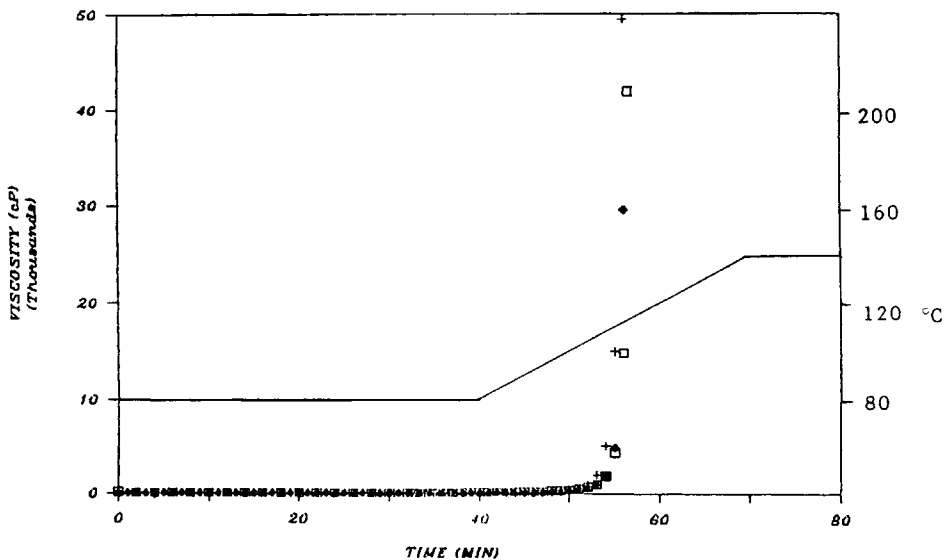


Fig. 12. Viscosity as a function of cure time. Comparison of experimental and predicted results of a simulated isothermal and dynamic cure cycle at $2^{\circ}\text{C}/\text{min}$ (\square - exp, $+$ - PHEN, \blacklozenge - MW).

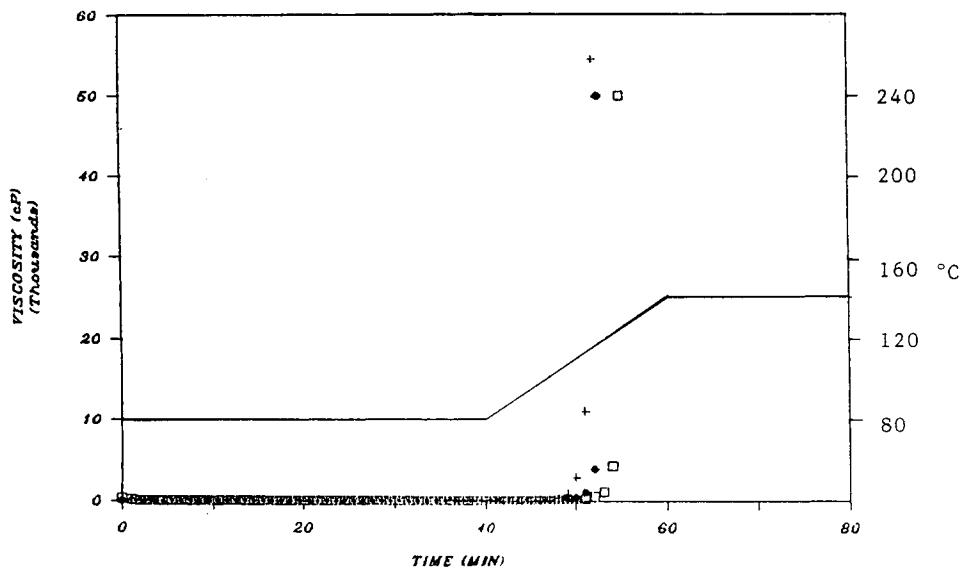


Fig. 13. Viscosity as a function of cure time. Comparison of experimental and predicted results of a simulated isothermal and dynamic cure cycle at $3^{\circ}\text{C}/\text{min}$ (\square - exp, $+$ - PHEN, \blacklozenge - MW).

different rates of $1^{\circ}\text{C}/\text{min}$ (Fig. 11), $2^{\circ}\text{C}/\text{min}$ (Fig. 12), and $3^{\circ}\text{C}/\text{min}$ (Fig. 13) to 140°C . The viscosity profiles show that both models predict the viscosity extremely well at heating rates of 1°C and $2^{\circ}\text{C}/\text{min}$. At $3^{\circ}\text{C}/\text{min}$, however as the system approaches the gel point, the branching theory model predicts the sudden viscosity increase better than the phenomenological model. The branching model prediction of the sudden increase in viscosity was off by only two minutes, while the phenomenological model had a discrepancy of four minutes. However, when compared over the entire cure cycle (55 min), the models differed little from each other.

Next, we studied two cases in which the polymer was ramped at $10^{\circ}\text{C}/\text{min}$ in order to evaluate the effect of a fast heating rate on the predictive capability of our models. The use of fast heating is of keen interest to the composites community because faster cycle cures could save processing time, energy, and costs. Figures 14 and 15 present the resulting two viscosity profiles for the advanced cure resin (initial extent of reaction was 18.8% in this case). The first cure cycle consisted of an initial ramp from 40 to 80°C at $10^{\circ}\text{C}/\text{min}$ which was then maintained at 80°C for 36 minutes, ramped again from 80 to 140°C at $10^{\circ}\text{C}/\text{min}$, and finally maintained at 140°C until cured. The resulting profile is shown on a semilog plot to emphasize any difference between the experimental and the predicted viscosity. The first cure cycle shows good agreement between both models with the phenomenological model predicting slightly higher viscosities at both ends of the cure cycle. The branching theory model shows excellent agreement with only a slight deviation during the initial five minutes. We emphasize here that the actual temperature lagged behind the programmed temperature, causing a continued decrease of viscosity in the early stages of the first isothermal period. But this discrepancy was detected and the actual temperature profile (not shown in

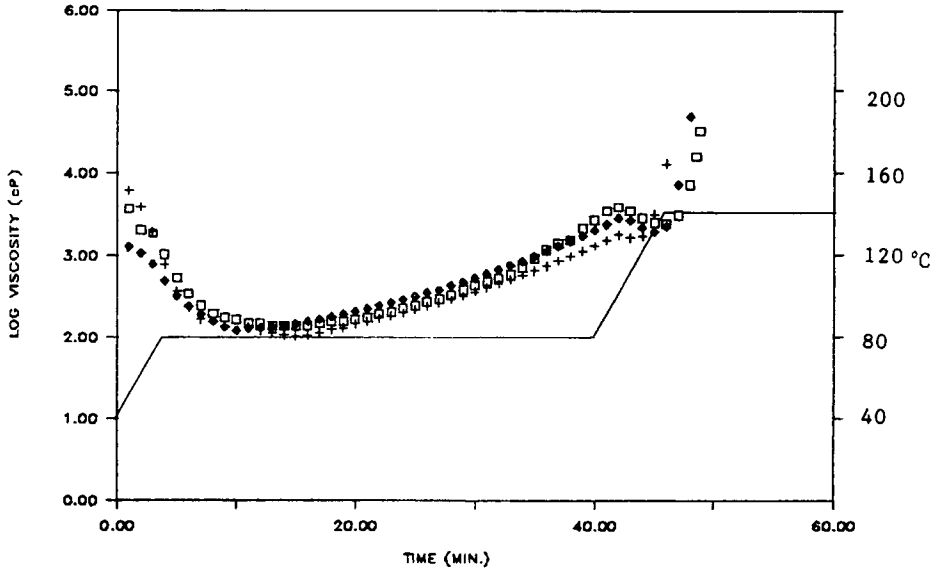


Fig. 14. Viscosity as a function of cure time. Comparison of experimental and predicted results of a simulated isothermal (80°C) and dynamic cure cycle at $10^{\circ}\text{C}/\text{min}$ (\square - exp, $+$ - PHEN, \blacklozenge - MW).

Figs. 14 and 15), obtained by the in situ measurements of resin temperature with a thermocouple, was used in calculations. The second cure cycle was the same as the first cure cycle, except that the first maintenance temperature was 90°C and the sample was kept at that temperature for 30 instead of 36 min. Again, both models predict the viscosity profile very well and again the

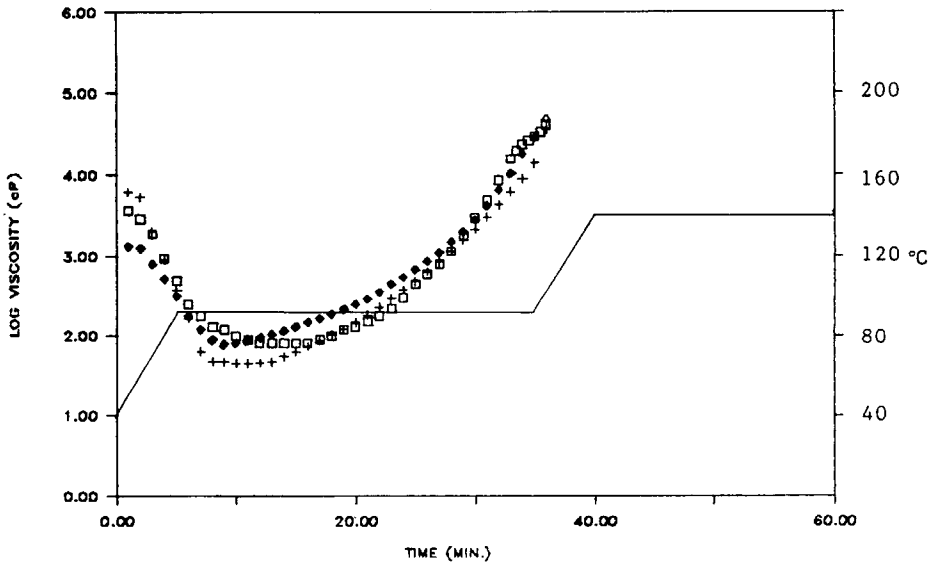


Fig. 15. Viscosity as a function of cure time. Comparison of experimental and predicted results of a simulated isothermal (90°C) and dynamic cure cycle at $10^{\circ}\text{C}/\text{min}$ (\square - exp, $+$ - PHEN, \blacklozenge - MW).

branching theory model is slightly more accurate than the modified WLF model, especially during the second ramp where the latter model predicts a sharp increase in viscosity while the former model accurately depicts even slight changes in the slope observed as the gel point is approached.

The advantage of the modified WLF model is that it is simpler to use once all the parameters are obtained and can be extended beyond the gel point. On the other hand, the modified WLF model predicts slightly less accurately the initial minimum viscosity and the viscosity near the gel point at high heating rates. The branching theory model describes the entire viscosity profile very accurately. Its only limitation is that it cannot be extended beyond the gel point.

CONCLUSIONS

A chemorheological study on an amine/epoxy system was completed. Use was made of the previously determined cure kinetics and the relationship between the glass transition temperature and the extent of reaction. A series of viscosity measurements were conducted for various isothermal and dynamic cure cycles. Two different models were used to predict the viscosity during cure and to check it against the experimental results; a phenomenological model based on a modified WLF equation and the branching theory model. In the former approach, information on cure kinetics in the form of T_g versus extent of reaction relationship was introduced in the WLF equation. It was also found that the parameters C_1 and C_2 varied at high cure temperatures ($T > 351$ K), but remained constant at low cure temperatures. The second modeling approach entailed the use of branching theory coupled with the cure kinetics information. Both models were found to give excellent agreement between experimental and predicted viscosities, with branching theory having an edge over the phenomenological equation, particularly in the region near the resin's gel point.

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