Modeling of Chemorheology of Thermoset Cure by Modified WLF Equation

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Synopsis

An analysis of chemorheology of cure of a formulation composed of diglycidyl ether of bisphenol-A (DGEBA) type epoxy resin and a mixture of aromatic amines was performed. A series of kinetic and rheological tests were run, and the experimentally obtained results were checked against the proposed model. A modified form of the classical Williams–Landel–Ferry (WLF) equation was used to model the chemorheology of the formulation. To arrive at the appropriate form of the modified WLF equation, expressions were developed for (i) the cure kinetics, (ii) the glass transition temperature as a function of the degree of cure, and (iii) the changes in parameters C_1 and C_2 as a function of temperature. By using these correlations in conjunction with the WLF equation, good agreement between predicted and experimental findings was observed.

INTRODUCTION

Within the last decade, modeling of chemorheology of thermosetting polymers has generated considerable interest among polymer scientists and engineers.[1,2] The impetus for those efforts was provided primarily by the ever-increasing use of thermosets as the matrix material in advanced composites. The most crucial aspect of processing of composites is the chemorheological behavior of the matrix resin, which is affected by the structural changes caused by cure reactions and by variations in molecular mobility induced by changes in temperature. The chemorheology of the matrix resin determines both the extent of reaction and the volume fraction of the matrix, which, in turn, determine the physical/mechanical properties of cured composites.

To establish a chemorheological model for thermoset cure, one must evaluate the time-dependent chemoviscosity as a function of the cure cycle and the cure kinetics of the resin formulation. Initial 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] Over the years, various modifications were made, primarily by introducing additional parameters while retaining the general form of the viscosity dependence.[2,10] Although useful, such models remain empirical in nature and are not readily related to the chemistry and the physical properties of the curing system. In modeling thermoset viscosity, others have taken into account 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 origin of

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those works dates back to the study by Flory of molecular weight distribution in nonlinear polymers.[14]

In recent years, several researchers have invoked the concept of free volume to calculate and predict the changes in chemoviscosity during cure.[15-19] Common to all those studies is the use of various modified forms of the classical Williams–Landel–Ferry (WLF) equation.[20] A modification of the WLF equation is necessary since the glass transition of the curing resin is a function of extent of reaction, and hence varies during the *in situ* polymerization. Thus the prerequisite for the application of the WLF equation to thermosets is the derivation of an accurate kinetic model. A modified form of the WLF equation, obtained in this study with experimental rhelogical and cure kinetics data, is shown to provide good agreement between predicted and experimentally obtained results.

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 in this study. This and similar formulations[17, 19, 21, 22] 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, the neat resin in our study was B-staged to the same extent of cure as in the prepreg. The main objectives of the reported research were (i) to develop a chemorheological model for the herein used formulation and (ii) to compare our results with other reported predictions of thermoset viscosity based on various modified forms of the WLF equation.

EXPERIMENTAL

Materials

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). 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 Co., 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,[24] who found that the formulation must first be B-staged, i.e., partially cured, to successfully process the prepreg. According to Claps, the formulation must be cured to approximately 20–25% conversion. The preparation of the B-staged resin started 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 min, 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.

Viscosity Measurements

The viscosity of neat and B-staged 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 programmable temperature controller. A SCA-21 spindle was used at a steady shear rate of 5.60 s^{-1}. The B-staged resin was prepared for the viscosity measurement according to the following procedure. First, the sample was preheated to 40°C and held 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. During this time, no further reactions took place. The minimum viscosity value was obtained after approximately 10–13 min into the run.

Differential Scanning Calorimetry

A DuPont 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 (DuPont thermometric standard). The first goal of our kinetic analysis was to determine the variation of the extent of reaction as a function of time and temperature. This was accomplished by an isothermal DSC analysis. The heat of reaction was determined by carrying the reaction isothermally to completion at the following temperatures; 80, 90, 100, and 110°C. Thermal equilibrium of the sample and reference holder was achieved in less than 30 s, and nitrogen gas was introduced into the DSC cell. A continuous curve was obtained showing the rate of heat generation for a given weight of sample as a function of cure time. The reaction was considered complete when the rate curve leveled off to the baseline. The total area under the exotherm curve, based on the extrapolated baseline at the end of the reaction, was used to calculate the isothermal heat of cure (H_{iso}) at a given temperature.

After the isothermal cure was completed, the sample was cooled rapidly in the DSC cell to 50°C. It was then heated at 10°C/min from 50 to 250°C in order to determine the residual heat of reaction (H_{res}). The sum of the isothermal heat, the residual heat, and the heat evolved during B-staging was taken to represent the ultimate heat of cure (H_{ult}). The reaction rate was determined directly from the DSC thermograms from the following equation:

$$\frac{d\alpha}{dt} = \frac{1}{H_{ult}} \frac{dH}{dt}$$

where α is the extent of reaction. To express the experimental results in terms of the extent of reaction (α), the DSC curves were integrated and the partial areas, as a function of time, were normalized with respect to H_{ult} and the sample weight.

The second goal of our kinetic analysis was to determine glass transition temperature of the curing formulation as a function of the degree of cure. A dynamic scan of an "as-mixed" sample was run first, yielding the reference

value of the total heat of reaction, H_T. The total heat of reaction was found to be 470 J/g. A series of samples were then prepared and cured in an oven at 80°C for various periods of time. At desired time intervals, samples were removed from the isothermal cure environment and quenched to arrest further cure. Dynamic DSC scans (10°C/min) were then run on the partially cured samples, and, from each thermogram, the corresponding glass transition temperature and the residual heat of reaction (H_R) were recorded. The difference between H_T and H_R was taken as the heat of reaction during the elapsed time period at 80°C. The degree of conversion from the dynamic DSC analysis was calculated according to the following equation:

$$\alpha = \frac{H_T - H_R}{H_T}$$

and a correlation between the extent of reaction and the corresponding glass transition temperature was established.

RESULTS AND DISCUSSION

In 1955, Williams, Landel, and Ferry expressed the variation of the viscosity of amorphous thermoplastic polymers with temperature (between the glass transition and 100 K above the glass transition) as

$$\log \frac{\eta}{\eta_g} = -\frac{C_1(T - T_g)}{C_2 + (T - T_g)} \tag{1}$$

where T_g and η_g (η_g is a constant with the value of 10^{13} cP) are the glass transition temperature and viscosity at that temperature, respectively, and C_1 and C_2 the characteristic constants which were originally assumed to have universal values.[20] Subsequent studies of amorphous thermoplastics have shown, however, that C_1 and C_2 are material-dependent but, for any given polymer, are not a function of temperature.[25, 26] It was also pointed out that the fractional free volume at glass transition and the coefficient of thermal expansion of the fractional free volume are related to C_1 and C_2.

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. Thus it is possible that, as the network structure changes, C_1 and C_2 vary with cure temperature and will hereafter be referred to as parameters instead of constants. Actually, Schneider et al. have recently argued that C_1 and C_2 in thermoplastic polymers should also be temperature-dependent.[27] Thus, if eq. (1) were to be used for the prediction of viscosity of thermosets during cure, one must account for the fact that (i) the glass transition temperature increases due to the network formation and hence must be evaluated as a function of the degree of cure; and (ii) the parameters C_1 and C_2 may vary with cure temperature, which can be established from viscosity measurements. These

two considerations necessitate incorporation of the following correlations into the classical WLF equation [eq. (1)]:

$$\alpha = f(T, t) \tag{2}$$

$$T_g = g(\alpha) = g'(T, t) \tag{3}$$

$$C_1 = h(T) \tag{4}$$

$$C_2 = i(T) \tag{5}$$

where α is the extent of reaction and the other parameters as previously defined. With eqs. (2)–(5), for any network structure during cure (as described by the extent of reaction), one can determine the corresponding values of T_g, C_1, and C_2. In this study, DSC analysis was used to determine eqs. (2) and (3) while C_1 and C_2 were calculated from the isothermal viscosity data from which eqs. (4) and (5) were subsequently generated by linear regression. Equations (2)–(5) were then substituted into eq. (1), resulting in a modified WLF equation which was utilized in this study in the following general form:

$$\log \frac{\eta}{\eta_g} = -\frac{C_1(T)\big[T - T_g(T, t)\big]}{C_2(T) + T - T_g(T, t)} \tag{6}$$

In eq. (6), the viscosity (or chemoviscosity) is a function of the cure time and temperature, and hence the degree of cure. We shall now proceed to describe how the correlations described by eqs. (2)–(5) were established.

Let us begin the discussion of our results by considering only those aspects of the cure kinetics of our formulation which are pertinent to this report. We have already published a detailed description of the kinetic analysis of several epoxy formulations from DSC data[22, 28] and will not repeat it here. Suffice it to say that an autocatalytic kinetic model of the following form,

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1 - \alpha)^n \tag{7}$$

was found to fit the data generated in this study very well. In the course of the development of the chemorheological model, our kinetic analysis was applied to arrive at an expression for the extent of reaction as a function of time and temperature. That correlation, whose general form is described by eq. (2), was deduced from experimentally obtained DSC runs on the B-staged resin. A plot of the extent of reaction as a function of time, shown in Figure 1, has the S-shape form which is characteristic of autocatalytic reactions and is in agreement with our earlier findings.[22, 28]

To establish a correlation between the extent of reaction and the corresponding glass transition temperature, samples were partially cured by heating in an oven for a specific period of time and then quenched into dry ice to arrest further reactions. From the subsequent scanning (dynamic) DSC run, the glass transition and the extent of reaction of the partially cured system were determined (as described in the Experimental section), and a relationship
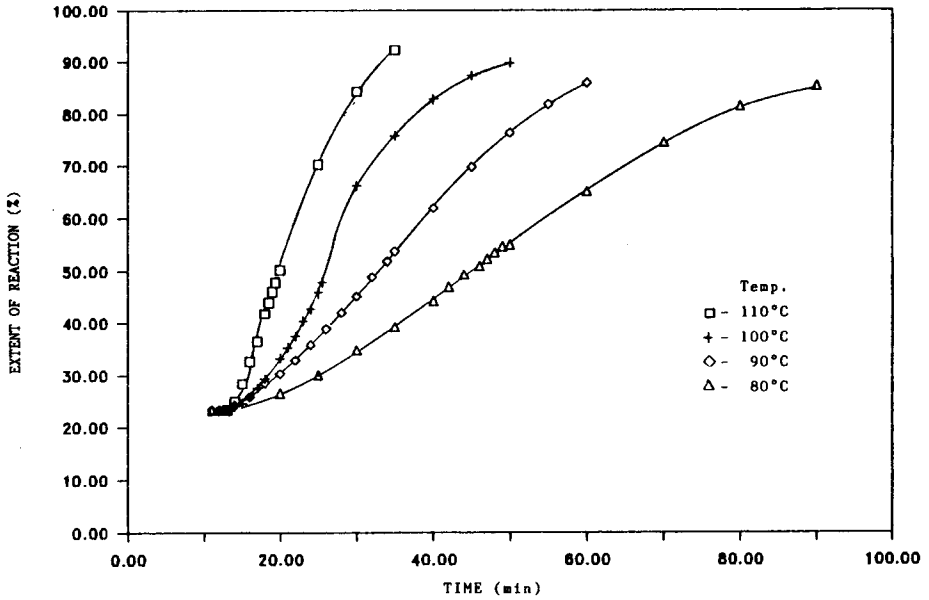
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Fig. 1. Extent of reaction as a function of time with cure temperature (°C) as a parameter: (□) 110; (+) 100; (◇) 90; (△) 80.
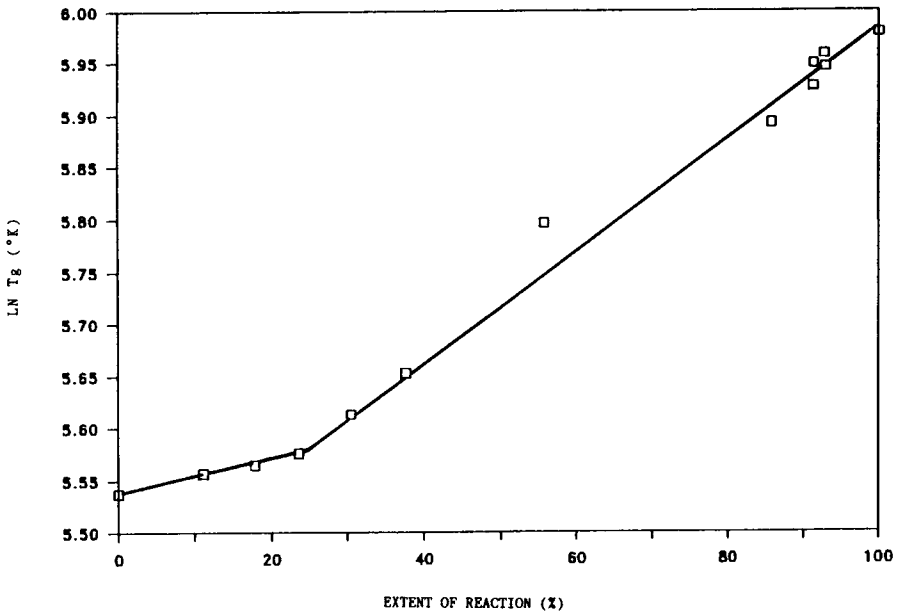

Fig. 2. Glass transition temperature as a function of degree of cure.

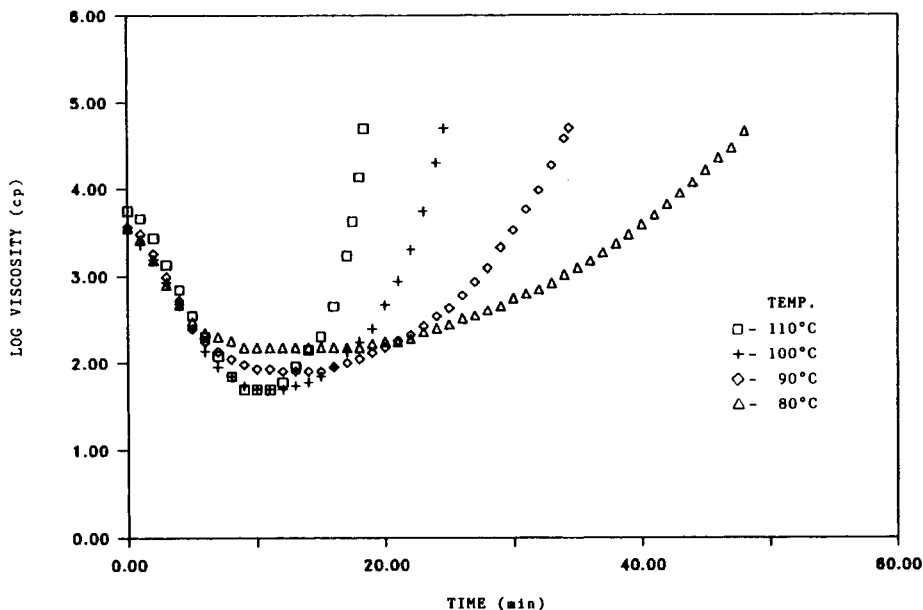Fig. 3.   Viscosity of B-staged resin as a function of time with cure temperature (°C) as a parameter: (□) 110; (+) 100; (◇) 90; (△) 80.

between these two parameters was established. 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:

$$T_g = \exp(1.590 \times 10^{-3}\alpha + 5.539) \quad \text{for } \alpha < 24\% \tag{3a}$$

$$T_g = \exp(5.628 \times 10^{-3}\alpha + 5.452) \quad \text{for } \alpha \geq 24\% \tag{3b}$$

Together, these two correlations describe the dependence of glass transition on extent of reaction, and represent the exact numerical form of eq. (3). 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]

Upon the completion of kinetic analysis, a series of isothermal viscosity measurements were performed, the results of which are shown in Figure 3. Due to the combined effects of temperature and chemical reactions on the molecular mobility of the curing system, two distinct viscosity regimes are seen for each sample, as clearly shown in Figure 3. The first regime starts from the point where the sample is ramped to its hold temperature and ends at the onset of isothermal hold. It was assumed that until the minimum viscosity is reached, the chemical reactions are negligible and the thermal effects dominate the molecular mobility, leading to the observed decrease in viscosity. The
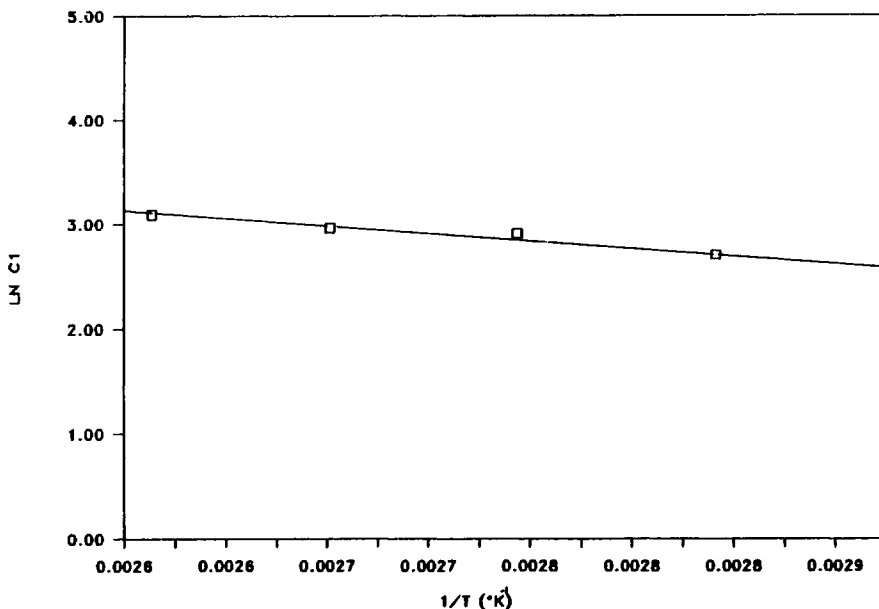
Fig. 4. C_1 as a function of temperature.

following equation was used to describe the first regime:

$$\log \frac{\eta}{\eta_g} = \frac{-13.51[T - (-8.9)]}{22.98[T - (-8.9)]} \tag{8}$$

with C_1 and C_2 having constant values since the glass transition temperature did not change in this region. The second regime, during which the viscosity increases, begins at the onset of cure (polymerization) and continues toward gelation and, eventually, vitrification. Our experimental runs were stopped before gelation which marks the formation of a 3-dimensional network of "infinite" molecular weight. It is interesting to note that the extent of reaction at gelation was independent of the cure temperature and approximately equal to 54% (α = 53% at 110°C; α = 54% at 100°C; α = 54% at 90°C, and α = 55% at 80°C). Furthermore, the extent of reaction was in the close vicinity of 57.7%, the value predicted by Flory's theory assuming a functionality of 4, which, in our system, corresponds to the number of active hydrogens per molecule of the curing agent.

Experimentally obtained viscosity data were now utilized to determine the parameters C_1 and C_2 [eqs. (4) and (5)]. For that purpose, eq. (1) was rearranged by plotting $T - T_g$ as a function of $T - T_g/\log(\eta/\eta_g)$. A linear dependence was observed for each temperature, allowing us to calculate C_1 and C_2 from the slope and intercept. When C_1 and C_2 were then plotted as a function of reciprocal temperature, as shown in Figures 4 and 5, they were found to have an Arrhenius-type dependence on temperature of the following
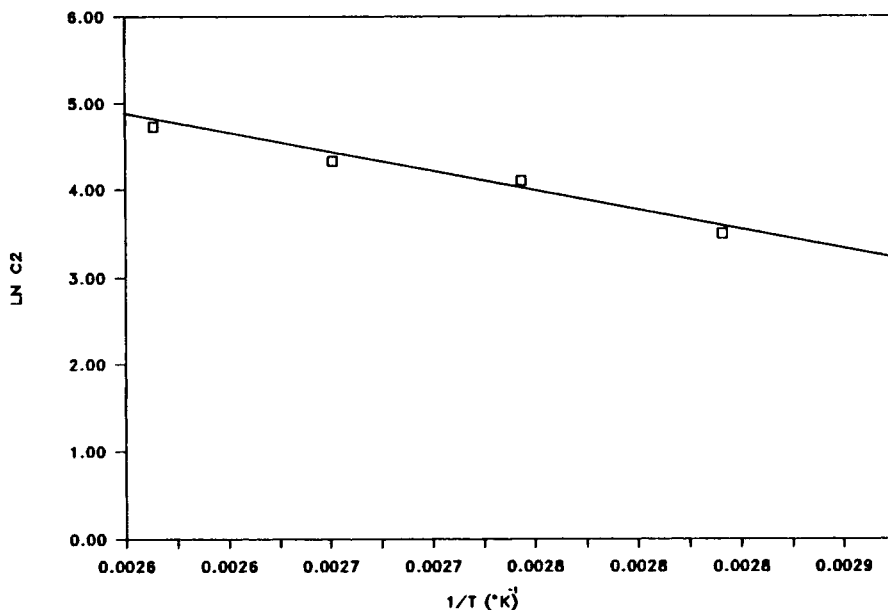
Fig. 5. C_2 as a function of temperature.

form:

$$C_1 = 1.66 \times 10^3 \times \exp(-1.65 \times 10^3/T) \qquad (4a)$$

$$C_2 = 1.18 \times 10^8 \times \exp(-5.30 \times 10^3/T) \qquad (5a)$$

where T is in degree Kelvin. These two correlations represent the exact numerical forms of eqs. (4) and (5), respectively.

At this point the glass transition temperature can be calculated for each cure temperature, knowing the corresponding degree of cure and using eq. (3a) or (3b). At that cure temperature, C_1 and C_2 can be obtained from eqs. (4a) and (5a). The predicted viscosity is then calculated using eq. (6). A comparison of predicted and experimental viscosity values shows good agreement, as clearly seen in Figure 6. It is evident that our model predicts equally well the viscosity decrease in the region governed by thermal effects, the minimum viscosity, and the subsequent increase in viscosity during cure. The slight discrepancy between predicted and experimentally obtained values in the minimum viscosity region is caused primarily by the diminished sensitivity of the viscometer at these low viscosity values.

As mentioned in the Introduction, several other researchers have reported the use of various modified forms of the WLF equation to predict the viscosity during cure. All other modification, however, differ from ours. For instance, Tajima and Crozier[15] studied the widely used commercial tetrafunctional epoxy resin formulation. They defined a new reference temperature, T_s, which is related to a simplified kinetic mechanism based on the rate of disappearance of the curing agent. Keeping C_1 and C_2 constant, an arbitrary choice of T_s was made to provide the best fit of data. A tetrafunctional epoxy formulation was
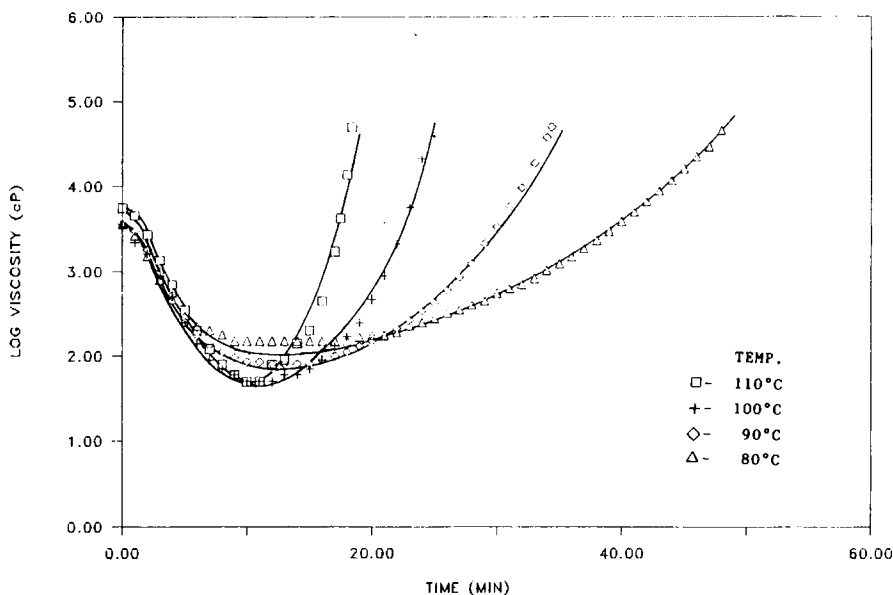
Fig. 6. Comparison of measured and predicted viscosity of B-staged resin as a function of time with cure temperature (°C) as a parameter: (□) 110; (+) 100; (◇) 90; (△) 80.

also studied by Apicella et al.[18] They modified the WLF equation by multiplying it with a preexponential molecular weight term based on Flory's[14] work, which is a function of the branching coefficient raised to the 3.4 power. But they offer little explanation about the choice of constants C_1 and C_2, the value of the exponent of the branching coefficient term, and the determination of glass transition as a function of extent of reaction. In their fine paper, Enns and Gillham[16] show how viscosity during cure can be calculated from an equation consisting of an Arrhenius term and a WLF term, the latter becoming applicable only at temperatures less than $T_g + 50°C$. The Arrhenius term contains the relationship between weight-average molecular weight and extent of reaction, which was previously derived by Macosko and Miller.[30] Unfortunately, viscosity–temperature data were not reported by Enns and Gillham. Instead a comprehensive table is presented, containing predicted gelation and vitrification times for various cure kinetic schemes. A comparison is made between the predicted results and the experimentally obtained data for an amine cured bifunctional epoxy formulation and good agreement was shown. In their modified WLF equation, however, C_1, C_2, and T_0 are all constants chosen to best fit the data. Chemoviscosity of an amine-cured bifunctional epoxy resin was also studied by Hou[17] in the low temperature range (22–34°C). In his model, C_2 was arbitrarily chosen as a constant ($C_2 = 51.6$), while C_1 was allowed to vary as a function of temperature. A computer analysis was then used to describe the advancement of cure in terms of the change of T_g with time. Several parameters were arbitrarily chosen to provide the best fit of data. Among them was the glass transition temperature of the as-mixed formulation (at time $t = 0$), which could have been easily measured. Golub et al.[19] recently reported the results of their study of an epoxy formulation similar to the one used in our work. An autocatalytic kinetic mechanism was

utilized to determine the extent of reaction as a function of cure time and temperature. A correlation between the glass transition temperature and the extent of reaction was then established using an equation proposed by Adabbo and Williams.[31] Golub et al. used numerical values for C_1 and C_2 of 17.44 and 51.6, respectively, while the other constants in their equation were obtained by the best computer fit of the data.

In summary, although based upon the same underlaying principle (i.e., modification of the WLF equation), our approach differs from the above-mentioned studies. The only assumptions made in this study were the constant viscosity at glass transition (η_g) and the absence of chemical reactions during the preisothermal heating ramp. All other parameters of our model were experimentally determined as a function of cure time and temperature. Development of correlations described by eqs. (2)–(5) for other epoxy formulations would be of interest as a necessary prerequisite for further generalization of our model.

CONCLUSIONS

A study of chemoviscosity of cure of an epoxy formulation was conducted. The system investigated is of interest as the matrix material in filament-wound composites. It was found that a modified form of the classical WLF equation can be used to accurately predict the change in viscosity (or chemoviscosity) during cure. The following supporting expressions were derived in the course of modification of the WLF equation. First, the kinetic analysis was performed, and an autocatalytic expression was found to compare well with the experimentally obtained results. Second, a correlation between the glass transition temperature and the extent of reaction was established from differential scanning calorimetry (DSC). And third, the parameters C_1 and C_2 of the WLF equation were found to vary as a function of temperature according to the Arrhenius form. The WLF equation, modified by the incorporation of these supporting expressions, was used to predict the viscosity during cure. A good agreement between predicted and experimentally obtained viscosity was observed.

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