Curing Kinetics and Chemorheology of Epoxy/Anhydride System

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ABSTRACT: The curing kinetics and chemorheology of a low-viscosity laminating system, based on a bisphenol A epoxy resin, an anhydride curing agent, and a heterocyclic amine accelerator, are investigated. The curing kinetics are studied in both dynamic and isothermal conditions by means of differential scanning calorimetry. The steady shear and dynamic viscosity are measured throughout the epoxy/anhydride cure. The curing kinetics of the thermoset system is described by a modified Kamal kinetic model, accounting for the diffusion-control effect. A chemorheological model that describes the system viscosity as a function of temperature and conversion is proposed. This model is a combination of the Williams–Landel–Ferry equation and a conversion term originally used by Castro and Macosko. A good agreement between the predicted and experimental results is obtained. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 3012–3019, 2003

Key words: thermosets, kinetics; differential scanning calorimetry; rheology; modeling

INTRODUCTION

The last two decades have produced a large increase in the number of applications of thermosetting resins, especially epoxy resins, in both traditional and newly expanding areas such as coatings, adhesives, electronics, and high performance composites.

In comparison with thermoplastics, the processing of thermosets and thermoset matrix composites is more complicated and less controlled because of their reactivity. In these processes polymer synthesis and shaping take place in a single operation, which involves the conversion of liquid monomers or prepolymers into a solid crosslinked polymer.

The mechanism and kinetics of cure determine the network morphology, which, in turn, dictates the physical and mechanical properties of the cured product.[1] Thus, understanding the cure kinetics of thermosets is essential for process development and quality control.

Perhaps the most important properties of polymeric materials in regard to their processing behavior are the rheological properties. Viscosity control during processing of thermosets is particularly critical because the viscosity varies not only with temperature and flow conditions but also with time because of polymerization reactions. Therefore, in order to control the curing effectively and to optimize the processing schedules and the properties of the finished product it is important to understand the relationship between the curing kinetics and rheological behavior.

Much work has been done to determine the appropriate models that best describe the cure kinetics and chemoviscosity of thermosets. Because of the complex nature of thermosetting reactions, phenomenological models are the most popular for these systems. The simplest are those based on nth order kinetics.[2–4] Another widely used model is the autocatalytic expression of Kamal and coworkers[5] that has been successfully applied to a variety of epoxy systems. Regarding chemorheological models, an advance was made from the batch-specific viscosity versus time or temperature correlations[6] to the models that include kinetic and/or structure information.[7–9] An extensive overview of the chemorheology of thermosets is reported by Halley and Mackay.[10]

The objective of this study was to characterize and model the curing kinetics and viscosity of a commercial low-viscosity laminating epoxy/anhydride system with the aim of optimizing the processing schedule. The system is especially suitable for wet filament winding, pultrusion, and injection molding The chemorheological study was performed by means of differential scanning calorimetry (DSC) and parallel-plate rheometry.

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EXPERIMENTAL

Materials

We studied a low-viscosity laminating system that is especially suitable for wet filament winding, pultrusion, and injection molding. The materials were supplied by Ciba Geigy Inc. and used as received. The system was prepared by mixing a bisphenol A epoxy resin (Araldite LY556), an anhydride curing agent (hardener HY 918), and a heterocyclic amine (accelerator DY 070). The mix ratio was 100/90/0.5 parts by weight (pbw). The pot life of this system at 23°C is between 165 and 175 h.

Characterization

DSC measurements

The calorimetric measurements were done on a Mettler TA 300 differential scanning calorimeter operating in the temperature range between −100 and 500°C in a nitrogen atmosphere. The sample size was around 15 mg. The dynamic DSC analysis was performed at three different heating rates of 3, 5, and 10°C/min. The sample was heated from room temperature to around 300°C. The total heat of reaction (H_T) is estimated by drawing a straight line connecting the baseline before and after the peak and integrating the area under the peak. Isothermal DSC experiments were performed at five temperatures ranging from 100 to 140°C in 10° increments. After each isothermal run the sample was rapidly cooled in the DSC cell to 30°C and then reheated at 10°C/min to 300°C in order to determine the residual heat of reaction (H_R). The digitized data were acquired by a computer and transferred to a PC for further treatment.

Measurements of glass-transition temperature

In order to determine the glass-transition temperature (T_g) as a function of the fractional conversion, a series of samples was cured in the DSC cell at 110°C for various periods of time. After each isothermal run the partially cured samples were rapidly cooled to −100°C and then subjected to a temperature scan from −100 to 300°C at 10°C/min to determine the glass-transition temperature and the residual heat of reaction. The glass-transition temperature was taken as the midpoint of the endothermic shifts observed during the rescans. The corresponding fractional conversion was calculated by means of the total and residual heats of reaction. Dynamic DSC experiments were also performed to determine the glass-transition temperature of an uncured (T_{g0}) and completely cured material ($T_{g\infty}$). To determine the latter the sample was heated from room temperature to 270°C at 10°C/min, rapidly cooled in the DSC cell to room temperature, and immediately reheated to 300°C at 10°C/min.

Rheometry

The rheological characterization of the system was carried out using a Rheometrics model RDS-II dynamic viscosity spectrometer. Disposable parallel plates with a diameter of 12.5 mm were used throughout. The oscillatory shear flow measurements were conducted under isothermal and dynamic conditions. Preliminary frequency and strain sweeps were carried out to determine the optimum experimental conditions. Isothermal experiments were performed under identical isothermal conditions as the thermocalorimetric measurements. The test fixture was preheated to the isothermal cure temperature and the plate spacing was zeroed. The chamber was then opened, the plates separated, and the resin sample rapidly inserted. The plates were then brought back together to a gap of approximately 0.2 mm. The chamber surrounding the plates was closed and the experiment initiated when the chamber returned to the set temperature (~2 min). An angular frequency (ω) of 10 rad/s and an initial strain of 10% were applied. As the cure proceeded, the strain was automatically adjusted to maintain the torque response within the range of the transducer. The viscoelastic properties of the sample during cure, including the complex dynamic viscosity (η^*), shear storage modulus (G'), and shear loss modulus (G''), were monitored. Other isothermal experiments were carried out at temperatures lower than 80°C to determine the viscosity of the uncured system. Several dynamic curing experiments at different heating rates were done as well.

Steady shear flow measurements were performed on samples at 120°C over a range of shear rates ($\dot{\gamma}$) between 100 and 10 s^{-1}. In the investigated range of shear rates, the viscosity was found to be independent of the shear rate up to the gel point.

RESULTS AND DISCUSSION

Analysis of DSC data

The average H_T was determined to be 365 J/g by computer integration of the dynamic DSC exotherm peaks. The total heat develop during isothermal tests (H_I) was comparable to the H_T obtained from dynamic tests only at 140°C. At all other investigated temperatures the H_I was lower than the heat developed during dynamic tests, and the H_I was an increasing function of the test temperature. Rescanning of the samples isothermally cured at temperatures lower than 130°C indicated residual reactivity. When the H_R was added to the heat developed in isothermal tests, the H_T value, which was comparable to the H_T from dynamic tests, was obtained. As is well known, these findings can be attributed to the influence of diffusion control on the reaction kinetics in the glass-transition region,[11] namely, the structural changes produced by the poly-
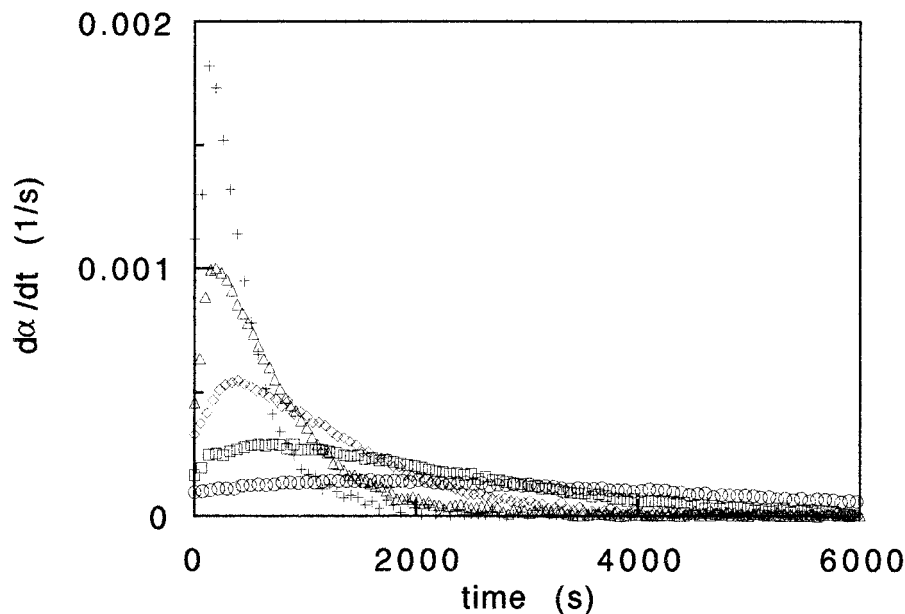
Figure 1   The isothermal reaction rate as a function of time at (○) 100, (□) 110, (◇) 120, (△) 130, and (+) 140°C.

merization reactions are associated with an increase of the T_g of the reactive system. When the increasing T_g value approaches the isothermal cure temperature, the molecular mobility is strongly reduced and the reaction becomes diffusion controlled and eventually stops. Subsequent exposure to temperatures greater than the previous isothermal cure temperature results in the increase of the molecular mobility of the polymer and further reaction. It is worth noting that a $T_{g\infty}$ of 134.6°C was determined.

Rate of reaction and conversion

The basic parameter governing the state of the material is the chemical conversion. Knowledge of the kinetic rate of curing and how the rate changes with the cure temperature is important and useful for predicting the chemical conversion achieved after a cure schedule.

The rate of reaction ($d\alpha/dt$) as a function of time (t) was calculated from the rate of heat flow measured in isothermal DSC experiments (dH/dt) by

$$\frac{d\alpha}{dt} = \frac{1}{H_T}\frac{dH}{dt} \tag{1}$$

The average value of the H_T developed during the dynamic DSC tests was taken as the basis for the ultimate fractional conversion. The rate of reaction as a function of time for different curing temperatures is shown in Figure 1. By partial integration of the areas under the curves in Figure 1, the fractional conversion (α) as a function of time was obtained (see Fig. 2).

$$\alpha = \frac{1}{H_T}\int\limits_{0}^{t}\left(\frac{dH}{dt}\right)dt \tag{2}$$

As described in the Experimental section, a series of uncured, partially cured, and completely cured samples were subjected to another temperature scan to determine the dependence of the glass-transition temperature on the fractional conversion. The fractional conversion of a partially cured sample was calculated as

$$\alpha = \frac{H_T - H_R}{H_T} \tag{3}$$

As Figure 3 shows, the glass-transition temperature of the investigated system increases with conversion following this simple relation:

$$T_g(\alpha) = 235.36 + 38.22\alpha + 142.58\alpha^2 \tag{4}$$

Kinetic modeling

The essential step in the study of cure kinetics by DSC is fitting of the reaction rate profiles, which are obtained from isothermal and dynamic experiments, to a kinetic model. As already mentioned, because of the complex nature of thermosetting reactions, phenomenological models are the most popular for these systems.
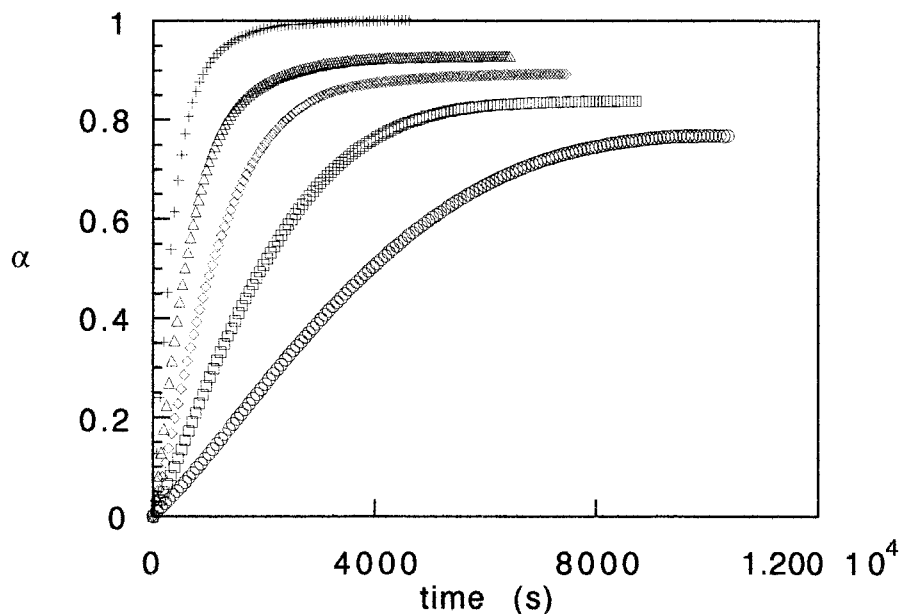
Figure 2 The isothermal fractional conversion as a function of time at ($\bigcirc$) 100, ($\square$) 110, ($\diamond$) 120, ($\triangle$) 130, and (+) 140°C.

For the kinetic behavior of the epoxy/anhydride polymerization, both first-order[12] and autocatalytic expressions[13,14] have been used to fit the experimental results. A simple model that explains both behaviors was recently reported in the literature.[15]

In this work the data were fitted to the modified Kamal et al.[5] kinetic model:

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(\alpha_{max} - \alpha)^n \qquad (5)$$

where α_{max} is the maximum fractional conversion at a given temperature needed to describe the vitrification phenomenon observed in isothermal cure.[16] The dependence of α_{max} on the cure temperature was fitted to a linear relationship. The parameters of the model k_1, k_2, m, and n were determined from each isothermal

thermogram by a nonlinear regression analysis (Microcal Origin 4.1). The overall reaction order ($m + n$) was assumed to be two. The m and n values were found to be relatively insensitive to temperature whereas the apparent reaction rate constants k_1 and k_2 increased with the temperature following the Arrhenius relationship,

$$k_i = k_{i0} \exp\left(\frac{-E_{ai}}{RT}\right) \qquad (6)$$

as shown in Figure 4. From the linear least-squares fit of $\ln k_i$ versus $1/T$ data, the preexponential factors (k_{i0}) and the activation energies (E_{ai}) were determined. The
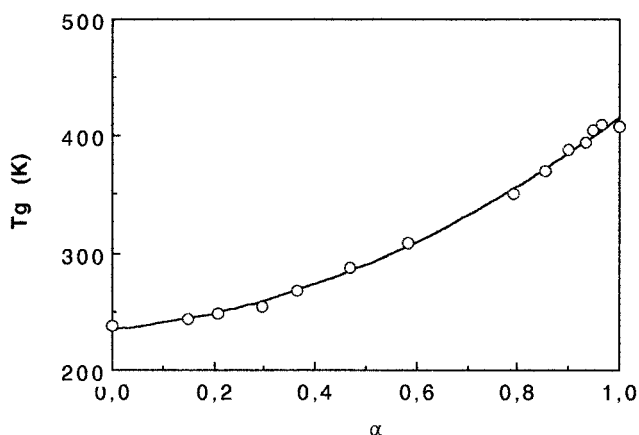

Figure 3 The glass-transition temperature as a function of the fractional conversion.
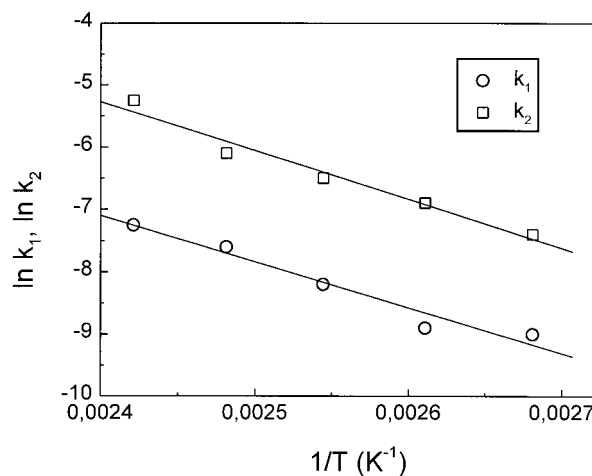

Figure 4 Arrhenius plots of the isothermal reaction rate constants.

TABLE I
Parameters of Kinetic Model [eqs. (5) and (6)]

Preexponential factor, eq. (6)	
k_{o1} (s^{-1})	$e^{10.7}$
k_{o2} (s^{-1})	$e^{12.6}$
Activation energy, eq. (6)	
E_{a1} (kJ/mol)	61.4
E_{a2} (kJ/mol)	62.1
m	0.64
n	1.36
α_{max}	$-1.43 + 0{,}00591T$

thermokinetic model parameters are summarized in Table I.

One of the drawbacks of isothermal curing is the limited temperature range in which useful kinetic information may be obtained. The modeling of industrial processing usually requires a knowledge of the curing kinetics in a broad temperature range. In order to see if the kinetic expressions arising from isothermal runs are valid outside the range of temperatures used for parameter fitting, the cure in dynamic conditions at constant heating rates was simulated as well. The expressions for k_1 and k_2 were substituted in the autocatalytic rate expression , which was solved numerically by the Runge–Kutta method for each investigated heating rate, to obtain the conversion and rate of reaction as a function of the time and temperature. Comparisons of the experimental data obtained in dynamic DSC runs at three different heating rates and the model predictions are presented in Figure 5. Excellent agreement between the calculation results and the experimental data in a broad temperature range is obtained. It is very encouraging that the behavior under both isothermal and dynamic conditions can be described with the same model over the temperature range that covers the usual processing conditions.

Analysis of rheological behavior during cure

In order to relate the viscosity of the reactive system to the reaction kinetics, the oscillatory shear flow measurements were performed under identical isothermal condition as the thermocalorimetric measurements. In the rheological characterization of thermosets the oscillatory shear flow measurements are preferred to those of the steady shear because they can be applied to a material not only in the liquid state but also in the rubbery and glassy states.

The isothermal complex viscosity (η^*) as a function of the reaction time is plotted in Figure 6. At the beginning of the cure, the viscosity slowly increases with time. Then, at a certain point a very rapid increase of the viscosity is observed. Gelation occurs during this stage. The following plateau in the com-
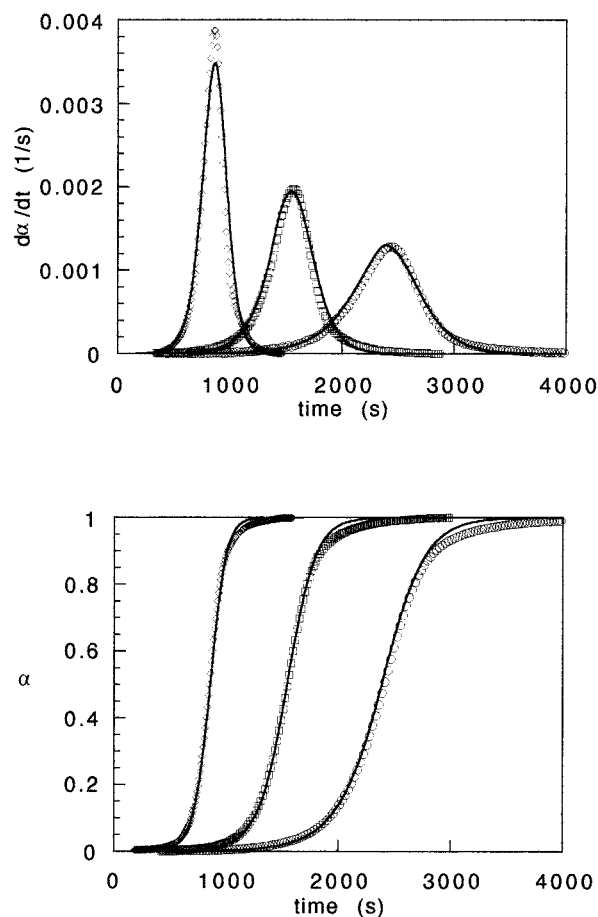

Figure 5 A comparison of (· · ·) experimental data with (—) the kinetic model data. The rates of (a) reaction and (b) fractional conversion as a function of time at heating rates of (○) 3, (□) 5, and (◇) 10°C/min. Zero time corresponds to the 30°C temperature.

plex viscosity with time is caused by the contribution from the dynamic modulus. In this region the material is no longer viscous.
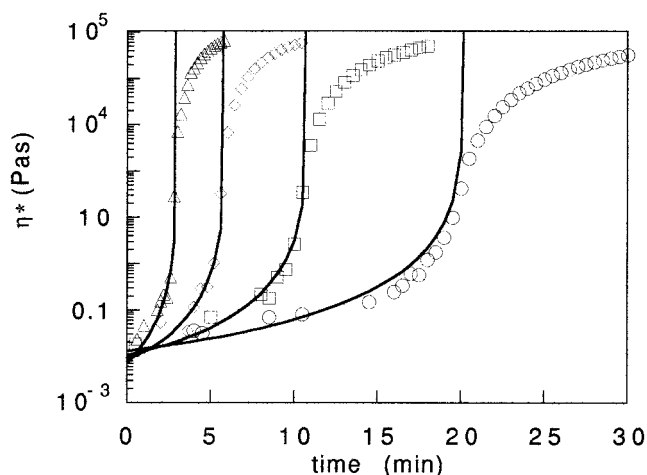

Figure 6 The complex viscosity as a function of time for isothermal cure at (○) 110, (□) 120, (◇) 130, and (△) 140°C. (—) The chemorheological model data from eq. (12).

TABLE II
Isothermal Gel Time (t_g) and Corresponding Fractional Conversion (α_g) at Different Temperatures

Temperature (°C)	t_g (min)	α_g
110	20.5	0.323
120	11.0	0.323
130	6.0	0.344
140	3.3	0.335

Steady shear flow measurements performed on samples at 120°C with a shear rate of 10 s^{-1} showed that the steady shear viscosity closely resembled the complex viscosity measured at a frequency of 10 rad/s [i.e., $\eta(\dot{\gamma}) = \eta^*(\omega)$], as predicted by the empirical Cox–Merz rule.[17]

Determination of gel point

Gelation corresponds to the incipient formation of an infinite network of crosslinked polymer molecules. From the processing standpoint, it is critical because the polymer no longer flows after the gel point.

The gel point, which is characterized by an infinitive value of the steady shear viscosity, is not easy to discern from the oscillatory shear flow measurements. Different criteria have been proposed in the literature such as the crossover point between the G' and G'' curves,[18] the inflection point of the G'' curve,[3] or the point where the loss tangent (tan δ) becomes independent of the frequency.[19–21] In this work gelation was assumed to occur when the rate of viscosity increase reached a maximum (when the second derivative of the curve showed a peak). The complex viscosity and divergence of the steady shear viscosity were found to be closely related for this case.

Combining the rheological data with the fractional conversion data obtained by means of DSC, the values for the fractional conversion at the gel point (α_g) were determined as reported in Table II. According to Flory's[22] gelation theory, gelation occurs at a fixed conversion as long as the reaction mechanism is not a function of the temperature. The deviation between α_g values for different isothermal experiments is on the order of 6%. To reduce the number of parameters, an average α_g value of 0.331 was assumed.

Viscosity modeling

Another aim of this work was to describe the viscosity behavior of the reactive matrix prior to gelation, as an aid to processing.

The effect of temperature on the system viscosity was analyzed first using the viscosity data measured in the range of temperatures where the reactions do not occur. Both an Arrhenius type equation and the

Williams–Landel–Ferry (WLF)[23] equation were applied to the data. It was found that the WLF equation,

$$\eta(T) = \eta_g \exp\left[-\frac{C_1(T - T_{g0})}{C_2 + T - T_{g0}}\right] \quad (7)$$

better describes the system viscosity, where T_{g0} is the glass-transition temperature of the uncured system, η_g is the viscosity at the glass transition, and C_1 and C_2 are constants that were determined from the rearranged WLF equation,

$$T - T_{g0} = -C_2 - C_1 \frac{T - T_{g0}}{\ln(\eta/\eta_g)} \quad (8)$$

as shown in Figure 7. The value of 10^{12} Pa s was assumed for η_g.[24]

In order to describe the effect of the structural changes (due to the occurrence of the polymerization reaction) on the viscosity, two existing chemorheological models were applied to the isothermal experimental data: the model proposed by Castro and Macosko[8]

$$\eta(T,\alpha) = \eta_0(T)\left(\frac{\alpha_g}{\alpha_g - \alpha}\right)^{A+B\alpha} \quad (9)$$

and a modified WLF equation[9]:

$$\ln\frac{\eta}{\eta_g} = -\frac{C_1(T)[T - T_g(T,t)]}{C_2(T) + T - T_g(T,t)} \quad (10)$$

From these studies the approach proposed by Castro and Macosko[8] was found to be more appropriate for the investigated system. As mentioned previously, the isothermal viscosity of the reactive system before the gel point has been related to the conversion obtained
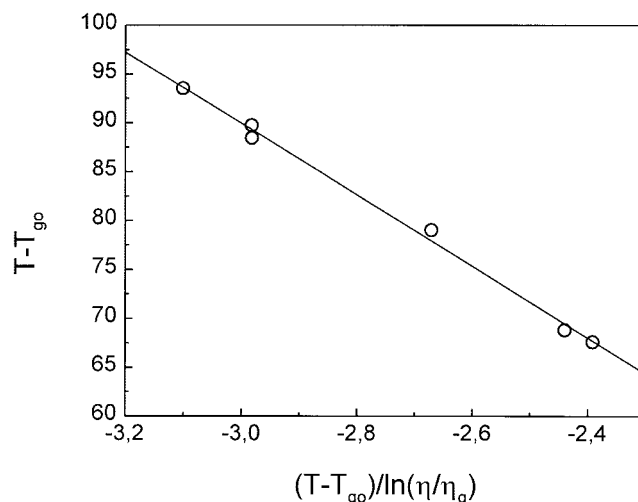

Figure 7 The determination of constants C_1 and C_2 of the WLF equation.
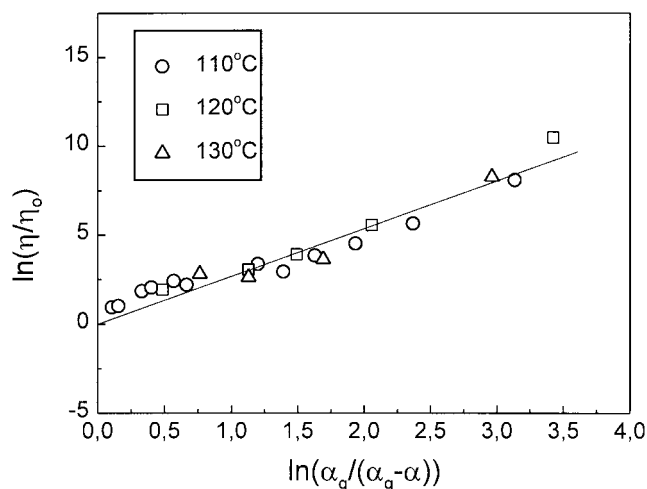
Figure 8 The reduced viscosity as a function of the conversion term $\alpha_g/(\alpha_g - \alpha)$ for isothermal tests at the reported temperatures.
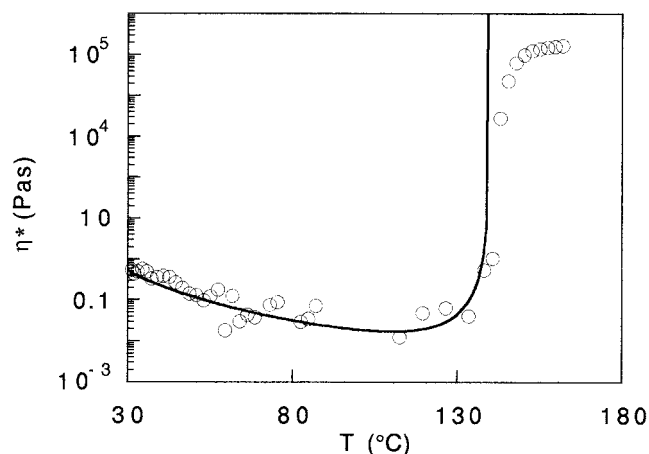

Figure 9 The complex viscosity as a function of temperature measured during a nonisothermal experiment at a heating rate of 4.6°C/min. (—) The chemorheological model data from eq. (12).

by means of DSC. When the η versus α data that correspond to different temperatures were plotted as the reduced viscosity (η_r) = η/η_0 (where η_0 is the initial viscosity at temperature T) versus the conversion term $\alpha_g/(\alpha_g - \alpha)$, a single curve was obtained. When shown in logarithmic form (Fig. 8), the data have a fair fit to a straight line passing through zero. Therefore, the isothermal viscosity of the investigated system can be described with an equation of the following form:

$$\eta(T,\alpha) = \eta_0(T)\left(\frac{\alpha_g}{\alpha_g - \alpha}\right)^n \quad (11)$$

From the slope of the linear plot shown in Figure 8, the exponent n in eq. (11) was determined to be 2.7. As follows from eq. (11), the viscosity becomes infinitely large at the gel point. Substituting the WLF equation[7] in eq. (11), the chemorheological model becomes the following form:

$$\eta(T,\alpha) = \eta_g \exp\left[-\frac{C_1(T - T_{g0})}{C_2 + T - T_{g0}}\right]\left(\frac{\alpha_g}{\alpha_g - \alpha}\right)^n \quad (12)$$

The parameters of the latter model are reported in Table III. In Figure 6 the comparison of the experimental data obtained during isothermal cure and the

model data are presented as well. A comparison of typical experimental results obtained under nonisothermal conditions at a constant heating rate and the results of modeling are presented in Figure 9. Note that the viscosity initially decreases as the temperature increases and the reactions are still not activated, but it reaches its minimum and then begins to increase because of the occurrence of the polymerization reactions. The model adequately describes the viscosity of the studied system in the unreacted state, as well as the minimum of the viscosity during nonisothermal cure. The agreement between experimental and predicted gelation limits is also good.

Because our developed model covers the wide range of temperatures that are usually included in a cure cycle, it could be an important tool in predicting the rheological behavior of the studied system during processing.

CONCLUSION

The chemorheology of a low-viscosity laminating system, especially suitable for wet filament winding, pultrusion, and injection molding, was studied by means of DSC and parallel-plate rheometry. The kinetic behavior of our system was described by a modified Kamal kinetic model accounting for diffusion-control effects. The kinetic model was verified through DSC tests performed at different heating rates. A chemorheological model was proposed that may be useful for predicting the viscosity variation during cure of our epoxy/anhydride system. The model is a combination of the WLF equation and a conversion term originally used by Castro and Macosko.[8] The prerequisite for its application is an accurate kinetic model. The chemorheological model was verified through rheological tests performed at different heating rates.

TABLE III
Parameters of Chemorheological Model

η_g (Pa s)	10^{12}
C_1	36.5
C_2	19.6
T_{g0} (K)	235.4
α_g	0.331
n	2.7

The theoretical predictions were found to agree fairly well with the experimental results.

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