Isothermal Rheokinetic Study of a Precured Resol Resin Beyond Gelation by Torsion

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ABSTRACT: The rheokinetics of the curing process of a resol resin was studied through isothermal analysis. The resin was subjected to a curing pretreatment until gelation was reached. Rectangular torsion was chosen as the appropriate strain form to carry out the study of the resin's curing kinetics, because the viscoelastic behavior of the material was closer to an ideal solid than to a Newtonian fluid. Seven operating temperatures were selected for analysis (80–110°C). The Arrhenius and Kiuna rheokinetic models were applied to the resin's complex viscosity (η^*) evolution during the crosslinking of polymer. The resol resin had curing activation energies of 62.6 and 65.8 kJ/ mol when the Arrhenius model was applied in four- and six-parameter forms, respectively. The Kiuna model was proposed to fit the nonlinear viscosity region found at the highest temperatures. This model was suitable to predict changes in the resin's complex viscosity, obtaining a curing activation energy of 69.5 kJ/mol for the resin. In addition, the evolution of the degree of mechanical curing was obtained from the elastic modulus, rather than from the more common DSC technique. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 2107–2114, 2012

Key words: resins; rheology; kinetics; gelation; torsion

INTRODUCTION

Phenolic resins have been applied in many commercial applications, such as household coatings, transformer components, and in electrical engineering and the automotive industry.[1,2] Phenolic resins are used for many applications, because they have properties such as excellent thermal stability, fire, high temperature and chemical resistances, ease and rapidity of curing, and low toxicity.[3] The rapid growth in the number of applications for phenolic resins has prompted extensive research. Thus, the importance of controlling the resin-curing process has become critical for obtaining the desired final properties of the material for specific applications. Studies of the mechanical curing kinetics of the resins improve knowledge of the processes involved during the crosslinking of the material and the quality of the final products, so that new materials can be developed.

Thermosetting resins are obtained from a highly exothermic polymerization reaction, where a mixture of monomers and other minor components such as curing agents, initiators, inhibitors, and catalysts react under heat. The curing of a resol resin is a complex process due to the changes in its physical properties along with chemical transformations; the initial polymer is converted into a three-dimensional crosslinked network (gelation).[4,5] The available volume in the molecular arrangement decreases as the reaction progresses, resulting in a lower mobility of the species and thus affecting resin viscosity. This results as the material's degree of cure overcomes gelation and approaches vitrification.[6,7] Vitrification is a reversible transition defined as the change from the liquid or rubbery state of a resin to the glassy state due to an increase in the crosslinking density and the molecular weight of the polymer, which may occur during the resin-curing process.[5]

Knowledge of a resin's curing kinetics is key to improving its final application. Thus, rheological characterization of the curing process of a thermoset polymer has great importance in production processes such as resin transfer molding (RTM) and is becoming a useful tool for developing process models and computer simulations to predict RTM process behaviors, which are closely related to the development of new materials.[8,9] The literature includes two different approaches to determining thermosetting curing kinetics: phenomenological or empirical, which is related to the overall reaction (macroscopic level),[10,11] and mechanistic, which examines each elementary reaction occurring during the process (microscopic level).[12,13]

Rheokinetic models have been classified by the rheological variables studied such as viscosity and complex viscosity when steady and dynamic rheological measurements are carried out, respectively.[14] Because of the high-transformation degrees of the materials reached during the performed rheokinetic analysis as the material approaches vitrification, a shift from a kinetic to a diffusion regime may be assumed.[15] The exponential evolution of rheological variables, such as complex viscosity (η^*), complex modulus (G^*), and elastic modulus (G'), decreases as the kinetics of resin curing move into the diffusion stage. The Kiuna model was suggested to describe the evolution of a resin's complex viscosity as diffusion phenomena increase in importance in the kinetics of the overall curing process and reduce the crosslinking rate. The Kiuna model adapted and improved upon the Fontana model by including non-Arrhenius viscosity dependence with a temperature term.[16]

The purpose of this work is to model the rheological behavior of a precured resol resin during its curing process to obtain a gelled material. The Arrhenius and Kiuna rheokinetic models are proposed to obtain good fits of the experimental complex viscosity studied under isothermal conditions. In addition, the beginning of a diffusion-controlled stage in the kinetics of the resin-curing process is determined through a critical value (α_{onset}) of the resol resin's degree of cure. Finally, the profiles of the resin's mechanical degree of conversion are calculated from the resin's elastic modulus. The agreement between the evolution of chemical and mechanical degrees of conversion for the material is confirmed.

EXPERIMENTAL

Materials

Hexion Specialty Chemicals Ibérica S.A® supplied the liquid phenol-formaldehyde resol resin. A precuring process was performed on the resin: it was poured into a steel mold, and a platen press was used (Collin® P300P). This mold (12 × 11.5 × 0.4 cm) was coated with a PET film (Goodfellow® ES301230), which was provided to protect the resin from foam formation during the precuring stage. The pretreatment of the material was optimized, and the operating conditions were set at 105°C, 100 bar for 23 min. The curing degree of the resol resin acquired was represented as α_{gel}.

Rheological runs

Rectangular 12 × 4 mm samples of the precured resin were cut with a rectangular die. Rheological runs were performed using an ARES Rheometer (TA Instruments®) with a rectangular torsion geometry.[17]

The resin samples were impregnated with high viscosity silicone (Dow Corning® 200 FLUID 60,000 cSt) immediately before the rheological test was carried out to avoid sample surface drying and oxidation of the material due to the dry air flow from the oven of the rheometer. Silicone is found in the literature as coating agent,[18] which was chosen among different possible inert agents such as water and glycerol, after performing time stability test that confirmed that it did not react with the resol resin. Throughout the characterization process of a resol, resin's curing process by rheological analysis has been carried out at three replicates produced in the platen press.

Chemical shrinkage of the resin took place during the curing tests.[19,20] The autotension rheometer option was enabled to prevent length/width rate changes and contact loss between the sample and the instrument geometry due to the material's chemical shrinkage. A 5-g axial tensional force was fixed at the beginning of the rheological run and kept constant by increasing the gap while heating to the operating temperature and reducing it as the resol resin isothermal crosslinking process advanced. The frequency applied was fixed at 1 Hz, and isothermal curing runs (80–110°C) were carried out for 30 min after the material reached the curing temperature. The initial temperature was 25°C, and a 20°C/min temperature ramp was programmed to approach the operating temperature. This procedure eliminated any temperature overshoot on achieving the isothermal temperature while minimizing the extent of resin-curing reactions during heating. The thermosetting polymer was analyzed after curing by a strain sweep from 0.01 to 1% at 60°C and 1 Hz to confirm that the rheological tests were carried out within the linear viscoelastic region of polymer.

Rheokinetic models

The Arrhenius model is the predominant empirical model to predict changes in the viscosity of a curing thermoset at any point in its time-temperature heating history.[21] In this work, the relationship between viscosity (η) and complex viscosity (η^*) was assumed to follow the Cox–Merz rule; therefore, rheokinetic models were applied to the resin's complex viscosity.[22] The four-parameter Arrhenius model for isothermal conditions is described by:

$$\mathrm{Ln}(\eta^*(t,T)) = \mathrm{Ln}\left(\eta_\infty^*\right) + \frac{\Delta E_\eta}{R \cdot T} + k_\infty$$
$$\times \int \exp\left(\frac{-\Delta E_k}{R \cdot T}\right) \cdot dt, \quad (1)$$

where η^* is the complex viscosity at absolute temperature T, η_∞^* is the reference viscosity at "infinite temperature," ΔE_η is the Arrhenius activation energy

for viscosity, t is the curing time, R is the universal gas constant, k_∞ is the kinetic constant analog of η_∞^*, and ΔE_k is the kinetic activation energy analog to ΔE_η.

Keenan[23] proposed a modified Arrhenius model that introduces a proportionality factor (ϕ) that was suggested to relate the extent of chain entanglement to the viscosity behavior during resin crosslinking. This model is described by eq. (2).

$$\mathrm{Ln}(\eta^*(t,T)) = \mathrm{Ln}\left(\eta_\infty^*\right) + \frac{\Delta E_\eta}{R \cdot T} + \phi \cdot k_\infty \\ \times \int \exp\left(\frac{-\Delta E_k}{R \cdot T}\right) dt. \quad (2)$$

A kinetic parameter was added to reduce the limitations revealed in some cases in the fitting of the resin's viscosity behavior developed by the Keenan model. The improved model treats the overall reaction order as an independent kinetic parameter. A six-parameter model including the reaction order (n) is described by eq. (3).

$$\mathrm{Ln}(\eta^*(t,T)) = \mathrm{Ln}\left(\eta_\infty^*\right) + \frac{\Delta E_\eta}{R \cdot T} + \frac{\phi}{n-1} \cdot \mathrm{Ln}(1+(n-1)) \\ \times k_\infty \cdot \int \exp\left(\frac{-\Delta E_k}{R \cdot T}\right) dt. \quad (3)$$

The kinetic parameters of resol resin curing in the four-parameter Arrhenius model [eq. (1)] were calculated by three consecutive single-linear regressions. The logarithm of the resin's complex viscosity was plotted versus time, and kinetic constants were obtained. The six-parameter Arrhenius model [eq. (3)] was applied to the resol resin using a least squares sum algorithm from Matlab® 2007 software to calculate the kinetic constants of the resin-curing process.

In the literature, several authors proposed kinetic models that quantify diffusion effects during the resin-curing process.[24,25] Commonly, a diffusion factor (f_d) is introduced into phenomenological models when diffusion is present.[26,27] This factor relates the kinetic constant for the overall process of resin curing to the kinetic constant for the chemically controlled stage. A critical value of the resin-curing degree (α_{onset}) is defined as the onset of diffusion becoming a relevant factor in the overall kinetics of the resin curing.

The Kiuna model was applied in this work to describe chemical- and diffusion-controlled stages.[28] Kiuna proposed a model based on the hypothesis that for isothermal situations, the viscosity may be represented in the dimensionless form $\alpha' = f(\tau)$, where α' represents the change viscosity with the curing process [eq. (4)].

$$\alpha' = \mathrm{Ln}\left(\frac{\eta^*}{\eta_0^*}\right). \quad (4)$$

η_0^* is the complex viscosity of the uncured resin at temperature T. Under isothermal conditions, the model predicts the rate of cure as $\alpha' = f(\tau)$. The function of $f(\tau)$ chosen, in the present work, is two order, as follows:

$$f(\tau) = \tau + a_1 \cdot \tau + a_2 \cdot \tau^2. \quad (5)$$

In addition, the basic isothermal relationship into the form $\tau = g(\alpha')$ can be inverted, where g is the inverse function of f. Thus, the equation is written in differential form $d\tau = g'(\alpha') \, d\alpha'$, where $d\tau = k(T)dt$ represents the increment of elapsed time. Finally, the general expression for the Kiuna model is given by eq. (6).

$$\frac{d\alpha'}{dt} = \frac{k(T)}{g'(\alpha')}. \quad (6)$$

$k(T)$, in the Kiuna model, is approximated by exponential fits according to the following Arrhenius equation:

$$k(T) = k_\infty \cdot \exp\left(\frac{-\Delta E_k}{R \cdot T}\right). \quad (7)$$

The Kiuna model also provides a viscosity polynomial dependence with temperature. To calculate the kinetic constants of the resin-curing process, by applying this model, a minimization algorithm of residual sum of squares from Matlab 2007 software was used.

RESULTS AND DISCUSSION

Determination of the diffusion-controlled stage onset

The evolution of the complex viscosity of the resol resin during the heating stage and the rheological isothermal runs (80–110°C) is shown in Figure 1. The lowest operating temperature (80°C) was fixed as the temperature that the resin began to show a significant increase in complex viscosity due to the curing process. The highest temperature was set at 110°C, because, at higher temperatures, the glass transition of the resin was reached within the 30 min curing time, and the material turned into a brittle material that broke during the rheological runs.

A decrease in the viscosity of the material was found within the 1–250 s heating ramp to the curing temperature due to the temperature dependence of the viscous flow term.[29] Once the temperature was reached (approximately at the point of minimum
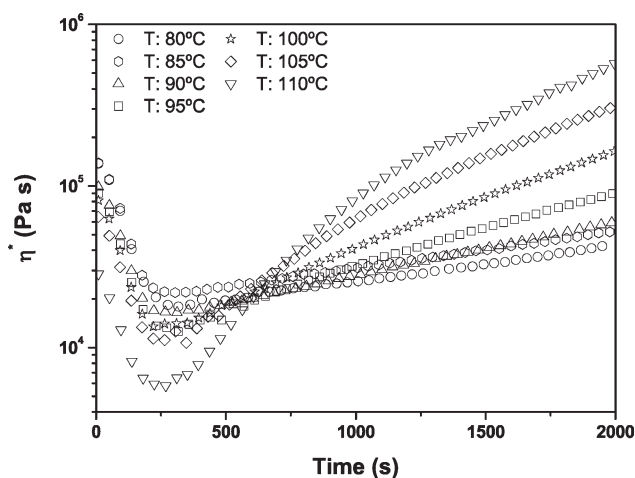
Figure 1 η^* versus time at all curing temperatures studied (80–110°C) for precured resol resin.

viscosity), the polymerization reactions proceed, and the complex viscosity began to rise as the molecular weight of the material increased.[4] In addition, we can also observe two zones with different slopes of complex viscosity versus time. In the first slope, the resol resin is curing up to reach the cure temperature equal to glass transition temperature. At this moment, the second slope is less pronounced due to a diffusion stage that begins to control the overall process kinetics of resin curing. Therefore, the kinetics of the curing process was controlled by diffusion rather than by a chemical reaction from a certain moment for each temperature assayed. To determine this moment, the onset time of the nonlinear evolution of the resin's complex viscosity (t_{onset}) was defined as a 5% deviation from the linear behavior, as shown in Figure 2 for a 110°C curing temperature. The onset of the nonlinear (on a semilog scale) behavior for the resin's curing degree
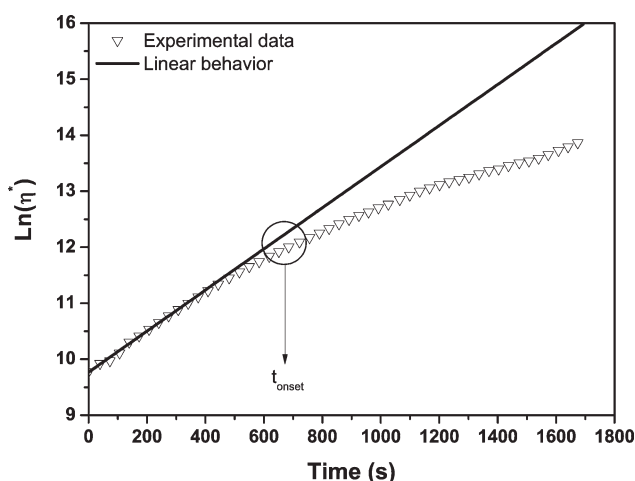
(α_{onset}) was obtained from the t_{onset} at each operating temperature.

The relationship between the curing temperature and α_{onset} is established by eq. (8).[6,30]

$$\alpha_{onset}(T) = p_2 \cdot \left(\frac{1}{T_2} - \frac{1}{T} \right), \qquad (8)$$

where p_2 is a fitting parameter, T is the curing temperature, and T_2 is the hypothetical critical temperature below which no chemical controlled reaction could occur ($\alpha_{onset} = 0$) when $T = T_2$. In eq. (8), the upper bound of α_{onset} is the unity. The parameters p_2 and T_2 were obtained by fitting the onset of the resin's degree of cure versus curing temperature, as shown in Figure 3 ($p_2 = 620.1$ K and $T_2 = 3.84$°C).

Rheokinetic modeling

The first rheokinetic model applied to the resin's complex viscosity was the four-parameter Arrhenius model. The logarithm of the measured and predicted viscosities at the lowest (80°C) and highest temperatures (110°C) tested are shown in Figure 4. Nonlinear (on a semilog scale) behavior was obtained at the highest curing temperatures ($\geq$95°C), and the fitting efficiency of the model is lower as the resin's final degree of cure reached increases. This phenomenon is due to a diffusion-controlled stage that overcomes the chemical control over the overall process rate, which takes place as the material approaches its glass transition temperature. This temperature reduces as the resin-curing degree increases, and, when it coincides with the operating temperature, the reaction stops entirely.

The kinetic constants of resol curing [$k(T)$] were obtained for each isothermal run according to Arrhenius temperature dependence. To obtain the kinetic parameters (E_k and k_∞) of the curing material, the
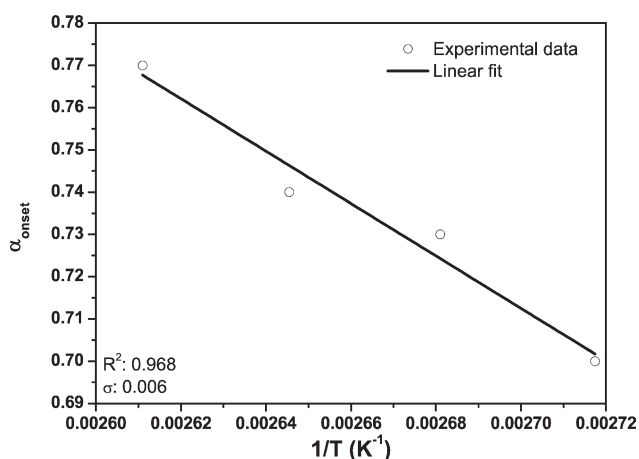

Figure 2 Experimental values and linear behavior of Ln η^* for the precured resol resin versus curing time at 110°C.

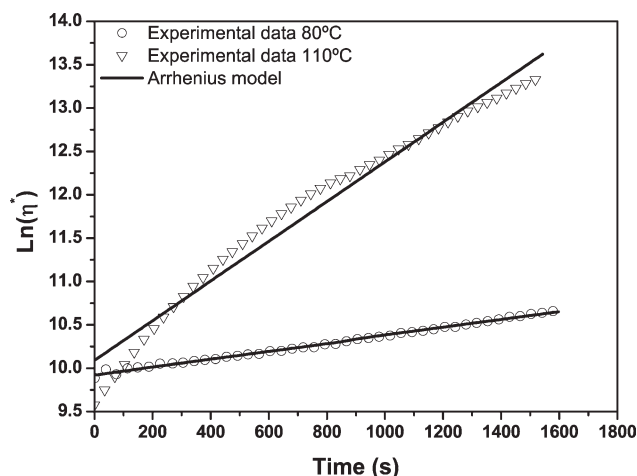**Figure 3** Values of α_{onset} for precured resol resin versus $1/T$.

Figure 4 $Ln(\eta^*)$ versus curing time for the Arrhenius model at 80 and 110°C.

logarithms of the kinetic constants were plotted versus $1/T$ as shown in Figure 5.

The kinetic parameters of resol resin curing, calculated by the simplest Arrhenius model, are exhibited in Table I. The E_k obtained was 62.6 kJ/mol, which is less than (70.7–96.3 kJ/mol)[31,32] or similar (53.4–64.3 kJ/mol)[33] to those found in the literature for this material. The Arrhenius model was not able to predict the nonlinearity in the resin's complex viscosity behavior. The goodness of the fits decreased as the operating temperature increased, as shown in Figure 4. An improved model becomes necessary to predict the viscosity behavior of the material at high curing temperatures. Thus, the use of the chain entanglement parameter (ϕ) is used for the later curing stages.

The six-parameter Arrhenius model was selected as a first approach to improve the modeling of non-linear behavior of the resin's complex viscosity.[29] The reaction order for the curing kinetics of this resol resin was found to be close to the unity when the DSC technique was used.[31] In Figure 6, the six-parameter Arrhenius model was applied to the logarithm of the resin's complex viscosity [$Ln(\eta^*)$]. The model showed suitable fits at high curing temperatures ($\geq$95°C), but the quality for the fits calculated at low curing temperatures decreased in relation to the four-parameter Arrhenius model. Nonlinear behavior of resin-curing process could be fitted, which decreases the efficiency of the model when just linear behavior occurs (Fig. 6).

The E_k obtained was 65.8 kJ/mol, which is less than (70.7–96.3 kJ/mol)[31,32] or higher (53.4–64.3 kJ/mol)[33] to those found in the literature for curing of resol resin. The chain entanglement parameter of phenolic resin was lower than the values proposed for an epoxy resin ($1 \leq \phi \leq 2$) by Dusi and May.[29] The variation of ϕ served to increase/decrease the

profiles by a constant value.[29] The reaction order of resin-curing kinetics was close to unity.

The most common four-parameter Arrhenius model was suggested to predict the resin's complex viscosity behavior at curing temperatures below 95°C. The use of the chain entanglement parameter (ϕ) in six-parameter Arrhenius model became necessary at higher operating temperatures.

The experimental and predicted values of $\alpha' = Ln(\eta^*/\eta_0^*)$ for the Kiuna model at 110°C are shown in Figure 7.

The predicted values for the resin's complex viscosity by the Kiuna model were suitable for both linear and nonlinear process regions, and the model was capable of predicting diffusion-stage of resin's complex viscosity. The kinetic constants $k(T)$ of the resol resin curing were calculated at each temperature, and an Arrhenius temperature dependence was assumed to obtain the activation energy of the process, as exhibited in Figure 8. The correlation coefficient increased considerably, and the standard deviation decreased significantly in relation to that of both Arrhenius models.

The activation energy calculated by the Kiuna model for the resin curing was 69.5 kJ/mol (Table I). This value was neared to those obtained by the six-parameter Arrhenius and Arrhenius models (65.8 and 62.6 kJ/mol, respectively). However, the Kiuna model provided an activation energy suitable for all of the tested temperatures. The E_k value for the resol resin obtained by the Kiuna model (69.5 kJ/mol) is lower than the values of activation energies found in the literature for other thermosetting resins such as novolac (60.8–117.8 kJ/mol),[34,35] epoxies (61.4–91.4 kJ/mol),[36,37] and polyurethanes (43.0–85.0 kJ/mol).[38] In relation to resol resin-curing process, the activation energy value obtained by applying the Kiuna model is less than (70.7–96.3 kJ/mol)[31,32] or higher
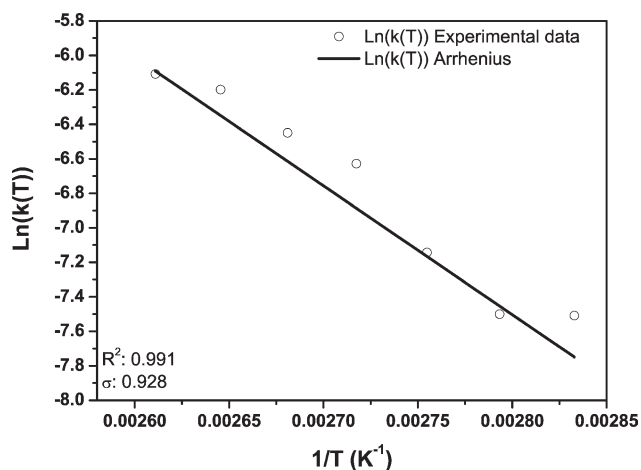

Figure 5 Experimental and predicted data of $Ln[k(T)]$ versus $1/T$ for resol resin through the 4p Arrhenius model.

Model	$-\Delta E_k$ (kJ/mol)	$\mathrm{Ln}(k_\infty)$	ϕ	n	σ	R^2
Arrhenius	62.6 ± 2.6	13.43 ± 0.83	–	–	0.928	0.991
Arrhenius 6p.	65.8 ± 1.7	14.57 ± 0.55	0.19 ± 0.08	1.04 ± 0.001	0.860	0.997
Kiuna	69.5 ± 3.9	16.20 ± 1.27	–	–	0.584	0.999

$(53.4–64.3 \text{ kJ/mol})^{33}$ to those found in the literature for curing of resol resin.

Rectangular torsion geometry was quite useful in the rheokinetic study of a resol resin, because it allowed the increase in operating temperature up to 110°C with respect to parallel plates geometry (shear strain), because the water content of the resin does not produce dispersion in the viscosity measurements. The main reason for using rectangular geometry is that the samples have larger free surface when compared with the disk used for shear strain analysis. In addition, rectangular torsion geometry allowed for cure shrinkage while maintaining consistent boundary conditions to investigate the post-gelation material behavior. In contrast, the achieved results for the activation energy of resol resin curing by applying the three models studied (62.6–69.5 kJ/mol) are lower than that obtained by shear strain $(72.1–88.1 \text{ kJ/mol}).^{39}$ The kinetic parameters obtained in this work are valid for a wide thermal region of the entire resin-cure cycle. Thus, this rectangular torsion geometry provided a better understanding of the development of material properties during the curing process of resol resin. This difference is due to the distinct geometry of samples subject to torsion or shear strain, which gives rise to different heat flows along them.
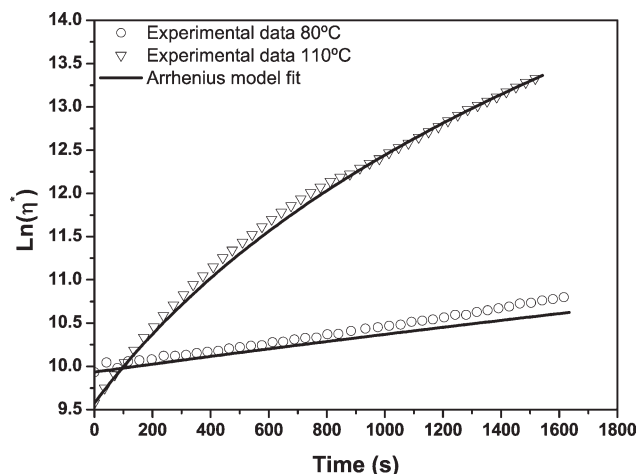
Profiles of the resin's mechanical curing degree

The profiles of the resin's curing degree can be calculated from a rheological variable such as the complex modulus (G^*), the elastic modulus (G'), or the resulting torque (Γ) value according to different authors.[40–43] In this work, we used the logarithm of the material's normalized elastic modulus to obtain the mechanical curing degree [$\alpha(t)$] of resol resin. The elastic modulus was chosen as a suitable rheological variable, because the high G' values found caused low dispersion in the measurements. The expression of $\alpha(t)$ is as follows:

$$\alpha(t) = \frac{\log(G'(t)) - \log\big(G'\big(t_{(\alpha=0)}\big)\big)}{\log\big(G'\big(t_{(\alpha=1)}\big)\big) - \log\big(G'\big(t_{(\alpha=0)}\big)\big)}, \qquad (9)$$

where α represents the mechanical curing degree, $G'(t)$ is the elastic modulus at time t, $G'[t_{(\alpha = 0)}]$ is the elastic modulus for the liquid resol resin, and $G'[t_{(\alpha = 1)}]$ is the elastic modulus for the fully cured resin.

The initial and final values of G' were measured for each test carried out. The initial degree-of-cure of the resin was $\alpha_{\text{gel}} = 0.65$, and the final degree-of-cure at each curing temperature was taken from a previous work in which was obtained by applying
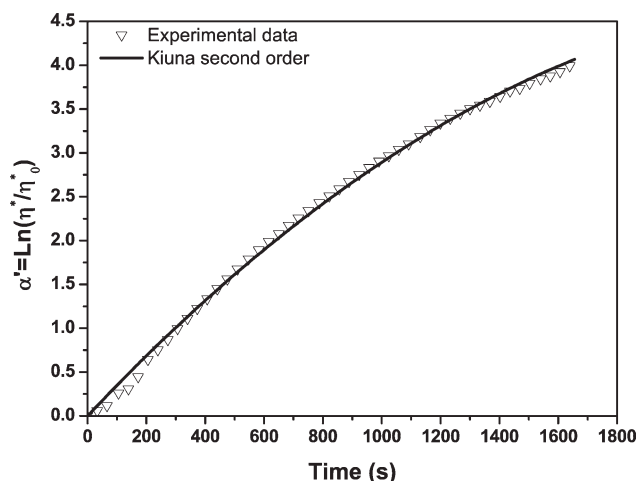

Figure 6 Experimental and predicted data of Ln(η^*) versus curing time for resol resin through the 6p Arrhenius model at 80 and 110°C.

Figure 7 Experimental and predicted values of α' versus curing time for resol resin, applying the Kiuna model at 110°C.

the Borchardt–Daniels' method.[31] The uncured and fully cured resin's elastic moduli {$G'[t_{(\alpha\,=\,0)}]$, $G'[t_{(\alpha\,=\,1)}]$} were calculated by substituting either the initial or final measured G' together with the initial or final degree-of-cure of the resin, respectively, in eq. (9). Finally, the evolution of the resin's curing degree was calculated by eq. (9) at different temperatures, as shown in Figure 9. A good agreement is observed between experimental and predicted values of $\alpha(t)$.

The mechanical profile for the degree of conversion was similar to the chemical profile obtained for resol resin curing.[31] The silicone fluid provided an environment where the reaction took place much like it did for samples under shear strain. The silicone isolated the material from the airflow supplied by the oven, protecting the resin and ensuring a constant temperature profile. The geometry of the samples is not relevant while the silicone fluid is either surrounding or coating the material. The viscosity of the silicone (100 and 60,000 cSt for shear and torsion strain, respectively) was important to optimize avoiding dripping. The phenolic resin studied, in these conditions, reacts similarly to a polyester resin studied by DMA and DSC techniques.[44]

CONCLUSIONS

The rheological behavior for the precured resol resin during the curing process can be described by the Kiuna chemorheological model. The four-parameter Arrhenius model can only predict the viscosity changes of precured resin when its curing kinetics was controlled by the chemical reaction stage ($T < 95°C$). The advantage of the six-parameter Arrhenius model and the Kiuna model in relation to the four-parameter Arrhenius model is that they are more suitable for fitting at high temperatures ($\geq 95°C$) and provide the reaction order of the resin curing. Both

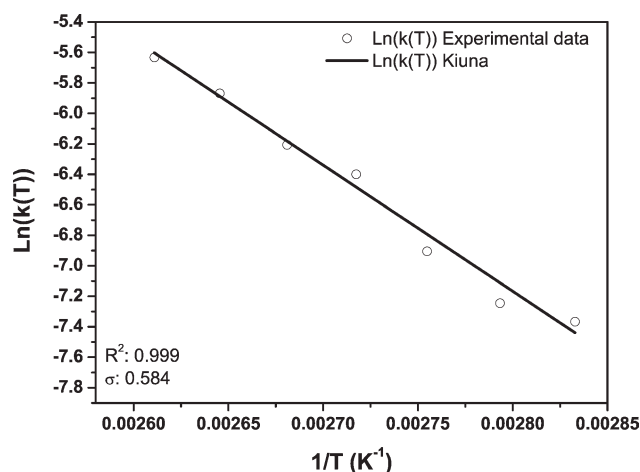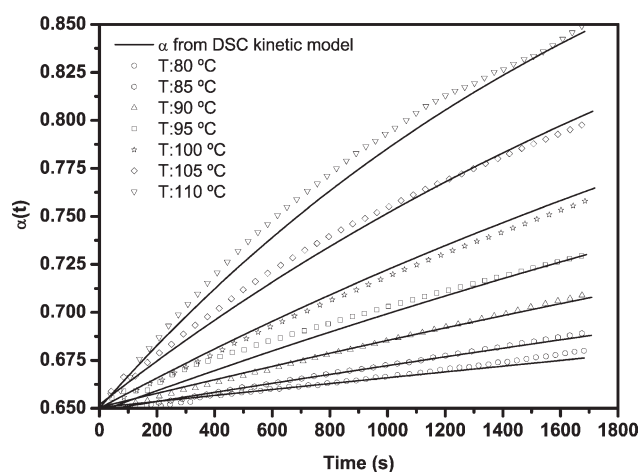**Figure 9** Degree of cure profiles of the resol resin calculated from the elastic modulus (G') and obtained from DSC measurements[37] versus curing time at different temperatures.

models successfully predicted the linear and nonlinear evolution of the resin's complex viscosity. We suggest the use of the Kiuna model, more simple, and valid to establish the diffusion stage in the control of overall process kinetics of resin curing at high temperatures.

The average activation energy obtained for the curing of a precured resol resin by applying the Kiuna model was 69.5 kJ/mol, a value slightly higher than those attained using four- and six-parameter Arrhenius models (62.6 and 65.8 kJ/mol, respectively) and close to those who can find in literature (53.4–96.3 kJ/mol).

Rectangular torsion was more suitable for the rheokinetic analysis of the resol resin-curing process than isothermal shear strain, because the torsion geometry allows increasing the operating temperature range and expanding profiles of the resin's curing degree. Finally, the profiles of the resin's mechanical degree of cure obtained at the operating temperatures tested were similar to the chemical degree of cure obtained by DSC.

Figure 8 Ln[$k(T)$] versus $1/T$ for the Kiuna model.

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