Rheokinetic of a Gelled Resol Resin Curing by Dynamic-Temperature Rheometry Based on Rectangular Torsion Strain

J. C. Domínguez, M. Oliet, M. V. Alonso, E. Rojo, F. Rodríguez

Departamento de Ingeniería Química, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, Avda. Complutense s/n, 28040 Madrid, Spain

ABSTRACT: The rheological behavior of a phenolic resol resin during its curing process was studied through a rheological dynamic-temperature analysis. Two heating ramps from 0 to 120°C (1°C/min) and from 0 to 150°C (5°C/min) were performed. The resin's complex viscosity data were obtained by applying a rectangular torsion strain. The overall change of complex viscosity with temperature was due to a combination of thermal softening, described by the Andrade equation, and the resin crosslinking process. The four- and six-parameter Arrhenius rheokinetic model was applied to the profiles obtained for the resin's complex viscosity, and the viscous flow and activation energies of curing kinetics were established. Two calculation methods are proposed to obtain the flow and curing parameters of the material. The six-parameter Arrhenius model was more suitable for predicting changes in the resin's complex viscosity, obtaining an activation energy of $\sim$ 38.0 kJ/mol for the resol resin curing process. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 5122–5129, 2012

Key words: resins; rheology; kinetics (polym.)

INTRODUCTION

Phenolic resol resins used as adhesives are usually in a fluid state at ambient temperature. Their more important properties are excellent thermal stability, fire resistance, high temperature resistance, chemical resistances, ease and speed of curing, and low toxicity.[1] Resol resin has been applied in many commercial applications, such as household coatings, electrical engineering, transformer components, and the automotive industry. For thermosetting systems in industrial applications, viscosity affects the processability of the resin. Rheology is used as a suitable technique for understanding the viscosity, the thermal softening and the curing behavior of the resin. In this study, chemorheology focuses on the rheological property changes during the crosslinking of the thermosetting polymer tested.[2] Understanding the chemorheology of a resin is important for optimizing operating conditions for a process that includes simultaneous reaction and viscous flow.[3] The flow of the resin is governed by its viscous history, which is dependent on the resin composition, the degree of cure, the curing chemistry, and the curing conditions.[4,5]

Cure kinetics of a thermosetting material allow for the evaluation of adhesive performance, the formulation of new materials, and the optimization of process parameters.[6] The curing processes of phenolic resins have been widely studied, especially by thermal analysis techniques.[1,7] This phenomenon is a complex process that affects the polymer's rheological behavior due to changes in the physical properties of the material. Such properties include the complex viscosity and the complex modulus.[8,9] Several chemorheological models that predict the evolution of these properties during polymer crosslinking and that provide the kinetic parameters of the curing process of thermosetting polymers have been developed.[2,5] Chemorheological models are formulated, classified, and suggested according to the variables studied, such as viscosity or complex viscosity, when steady and dynamic rheological measurements are carried out, respectively. One of the most relevant rheokinetic models found in literature is the Arrhenius model,[2,5,10–13] which is proposed in this work as a four- and six-parameter model.

Linear and nonlinear least squares algorithms are often found in the literature as a useful tool to calculate the kinetic parameters of a resin curing process when experimental data are applied to a model.[14–16] In this work, a nonlinear least squares fitting

algorithm was employed in order to calculate the rheokinetic parameters of the resol resin's curing process by applying the Arrhenius model.

Rheological analysis of resin crosslinking has been performed mostly under isothermal operating conditions, and studies of rheological behavior of a resol resin during its curing process has not been extensively used under dynamic temperature conditions. However, nonisothermal rheological assays provide, in a single run, the viscous flow and curing kinetic parameters of the resin curing process, thus reducing the necessity for multiple test analyses used in isothermal studies. Additionally, dynamic rheological analysis offers a quantitative overview of the adhesion mechanics from which the gelation, and vitrification points may be inferred.[17,18] The main drawback of the dynamic analysis is the overlapping of flow and crosslinking phenomena and the dependence of the material's complex viscosity profiles on the heating rate during periods when diffusion rate controls the kinetics of curing.

The study of resol resin's curing process under nonisothermal conditions using shear strain was published in a previous work.[19] In this work, a new study of the resol resin's curing process using a rectangular torsion strain under nonisothermal conditions was performed. The type of strain applied to the samples, as well as the temperature range, sample size and heating rates used, differ from the previous nonisothermal work.

The goal of this study is to obtain the rheological behavior of a resol resin subjected to a nonisothermal curing process, to propose the best rheokinetic model that describes the resin's complex viscosity evolution, and to suggest a proper calculation methodology for determining the flow and kinetic parameters of the four- and six-parameter Arrhenius model. Common parallel-plate geometry in the rheometer did not permit water vaporization and a significant shrinkage and nonuniform curing under the plates occurred, especially during the later stage of resin curing, so a rectangular torsion strain was used in a rheometer.[6]

EXPERIMENTAL

Materials

The resol resin was supplied by Hexion Specialty Chemicals Ibérica S.A. The main properties of resin were as follows: free phenol content ($<0.2\%$), viscosity (25°C, 275–475 cP), and a solids content range of 45–47%. The gel time of the resol resin studied was between 9 and 10 min. The gel time for resin samples was measured in a Gel-Time-Apparatus at 130°C in accordance with ISO 9396 B. The liquid resin was placed in a test tube and equipped with a plunger, which was moved up and down while the resin is still liquid. When the material reached its gelation, the measuring sensor was stopped.

Sample preparation

A precuring process was applied to the liquid phenol-formaldehyde resol in a laboratory platen press (Collin® P300P). The resin was poured into a steel mold designed to obtain a $12 \times 11.5 \times 0.4$ cm³ precured sample. The mold was coated with a PET film (Goodfellow® ES301230) to protect the resin from foam formation during the precuring stage. The pretreatment of the material was optimized to reach the resin's gel point, and the operating conditions were 105°C and 100 bar for 23 min. The resin curing degree (α) at the gel point is 0.65.[20]

Rheological runs

Rectangular (12×4 mm²) 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. The resin was coated by a high viscosity silicone (Dow Corning 200® FLUID 60000 cSt) to avoid drying of the material surface and/or the oxidation of the resin due to the dried air flow from the convection oven. The air was applied to the resin in order to set the required operating temperature. Changes in the resin's length due to the thermal expansion and chemical shrinkage of the material were measured, and the gap was changed to avoid contact loss between the sample and the rheometer as well as to keep constant initial axial tensional force of 5 g applied to the sample.[21–23] Frequency application was fixed at 1 Hz and two heating ramps (1 and 5°C/min) were carried out from 0 to 120°C and from 0 to 150°C, respectively. The highest temperature was restricted to 120 and 150°C in order to avoid thermal degradation processes of the material, reaching a resin's final curing degree of 0.68 and 0.70 for each temperature, respectively.[24,25] Strain sweeps were carried out after each curing test at 60°C, 1 Hz, and a strain range from 0.01 to 1% in order to ensure that the resin samples were always within their linear viscoelastic regions. This temperature was chosen due to the resin's maximum degree of cure was already reached and curing rate was stopped at this temperature, which was over resin's T_g.

Chemorheological models

In this work, the Arrhenius model was proposed to describe changes in the resin's complex viscosity due to thermal level increases, to describe the resin curing process, and to describe a combination of

both phenomena. The rheokinetic model was applied to the profiles of the resol resin's complex viscosity. The Arrhenius model was originally a four-parameter model as shown in eq. (1), where η_0^* is the flow constant for the complex viscosity dependence on temperature (of thermal-softening stage) of the gelled resin, and $k(T)$ is the kinetic constant for the resin's postgel curing process at certain temperature, T.

$$\ln(\eta^*(t,T)) = \ln(\eta_0^*(T)) + \int k(T) \cdot dt \qquad (1)$$

The Arrhenius chemorheological model is composed of two terms, the Andrade expression [eq. (2)] that predicts the common decrease of the complex viscosity for solids and liquids due to temperature and the curing kinetic term that describes the increase of the complex viscosity due to the rising of the crosslinking density of the resin during its curing process [eq. (3)]. In eqs. (1)–(3), η^* is the resin's complex viscosity at absolute temperature T, η_∞^* is the reference complex viscosity at "infinite temperature," ΔE_η is the activation energy for viscous flow, t is the curing time, R is the universal gas constant, k_∞ is the kinetic constant analogue of η_∞^*, and ΔE_k is the activation energy of resin's curing kinetics.

$$\ln(\eta_0^*(T)) = \ln(\eta_\infty) + \frac{\Delta E_\eta}{R \cdot T} \qquad (2)$$

$$k(T) = k_\infty \cdot \exp\left(\frac{-\Delta E_k}{R \cdot T}\right) \qquad (3)$$

Keenan proposed a modified Arrhenius model introducing a proportionality factor (ϕ), which was suggested to relate the amount of chain entanglement with the viscosity behavior during the resin crosslinking.[26] This model was developed by adding a new parameter to reduce the limitations occasionally revealed for the fitting of a resin's complex viscosity data. The improved model treats the overall reaction order as an independent parameter. A six-parameter model including the reaction order (n) is described by eq. (4).

$$\ln(\eta^*(t,T)) = \ln(\eta_\infty^*) + \frac{\Delta E_\eta}{R \cdot T} + \frac{\phi}{n-1} \cdot \ln(1 + (n-1))$$
$$\cdot k_\infty \cdot \int \exp\left(\frac{-\Delta E_k}{R \cdot T}\right) \cdot dt \quad (4)$$

To apply the Arrhenius model to the evolution of the resin's complex viscosity during curing, we propose two calculations methods:

- Method 1: Flow (ΔE_η, $\ln(\eta_\infty^*)$) and curing parameters ($-\Delta E_k$, $\ln(k_\infty)$, ϕ, n) of the Arrhenius model were calculated simultaneously by applying a nonlinear least squares fitting algorithm

(Matlab® 2007) when the model was applied to the resol resin's complex viscosity data.
- Method 2: Flow parameters, ΔE_η and $\ln(\eta_\infty^*)$, were calculated by selecting the linear decreasing stage of the material's complex viscosity data, which corresponds to the thermal softening stage, and fitting them to the Andrade equation by linear regression (Origin® 8.0). The resin curing parameters provided by the Arrhenius model ($-\Delta E_k$, $\ln(k_\infty)$, ϕ, n) were obtained by applying the kinetic model to the complete profile measured for the resin's complex viscosity vs. temperature using a nonlinear least squares algorithm and taken the flow parameters calculated previously.

RESULTS AND DISCUSSION

The evolution of the material's complex viscosity during the nonisothermal rheological runs, 0–120 and 0–150°C for 1 and 5°C/min heating ramps, respectively, are shown in Figure 1.

Three different stages were determined for the material's viscosity behavior during the rheological analysis as described Halley and Mackay[2] for dynamic temperature tests. The first stage (from 0 to 30°C and from 0 to 50°C for 1 and 5°C/min, respectively) showed the resin's complex viscosity dependence on temperature, described by the Andrade expression. The reactions were still not activated; therefore, the material's complex viscosity decreased as temperature increased.[27] For high operational temperatures, 90 to 120°C and 110 to 150°C, the resol resin's complex viscosity showed an exponential increase due to the advance of the crosslinking process and the rise of its molecular weight.[6,8] Finally, a stage where both phenomena, temperature softening and curing process of resin, overlapped was found from 30 to 90°C and 50 to 110°C for each heating ramp assayed. The minimum value obtained for the complex viscosity of the material was reached at 60 and 90°C for 1 and 5°C/min, respectively. This minimum value of the complex viscosity becomes a key value during the design of a resin's cure cycle. When the complex viscosity of a resin reaches the minimum value during its processing, the trapped bubbles must be allowed to leave the polymer, which becomes mobilized as the viscous flow forces are sufficiently large to overcome the surface tension forces.[27] The temperature at the complex viscosity minimum increased for the highest heating rate, a phenomenon that has been widely reported when using thermal analysis techniques.[28–30] In addition, an exponential dependence of the minimum viscosity with the heating ramp used was found by Martin
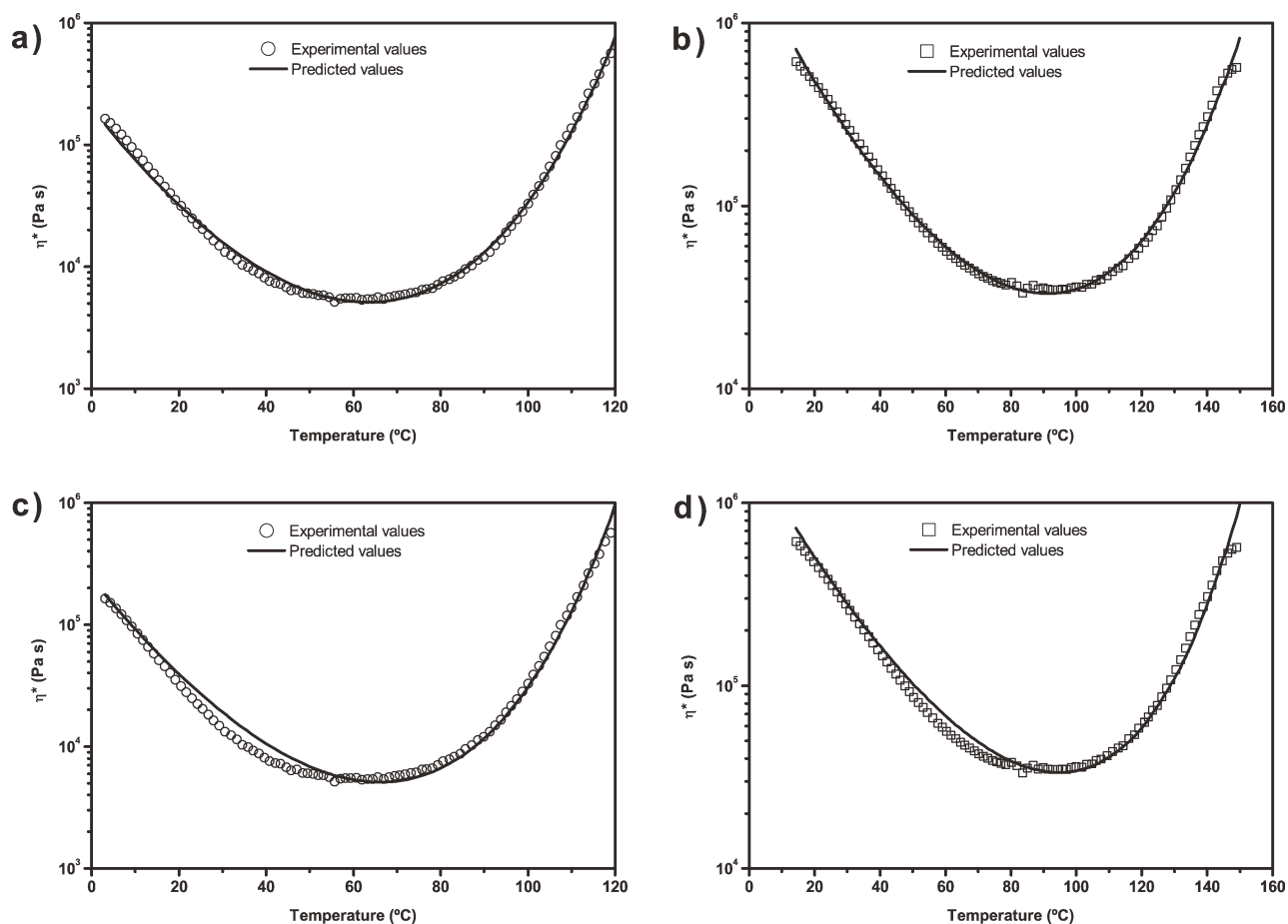
Figure 1 Experimental values of resin's complex viscosity and those predicted by applying the Arrhenius model versus temperature. first method: (a) 1°C/min, (b) 5°C/min; second method: (c) 1°C/min, (d) 5°C/min.

et al. when studying the nonisothermal curing of thermosetting resins by rheological analysis.[4]

The resin curing process rate was controlled by the crosslinking reaction during the tests for all samples. This is shown by the linear behavior of the material's complex viscosity. Thus, the heating rates applied to the resol resin were high enough to avoid the control of overall process kinetics by diffusion, which is commonly observed during the rheological tests that obtain nonlinear behavior for the resin's complex viscosity. This nonlinear behavior occurs as the material approaches vitrification at each curing temperature. Typically, diffusion control is concurrent with vitrification of the polymer, and it has been observed in the rubbery region when T_g is within 10–20°C of the cure temperature.[31] Therefore, during each heating ramp used, T_g was never close to the operating temperature. In addition, the absence of a decrease in the resin's complex viscosity during the third stage proved that no degradation processes take place at the highest operating temperatures chosen for each heating rate.[24]

The four-parameter Arrhenius chemorheological model, eq. (1), was applied to data of resol resin's

complex viscosity. The parameters of the model, flow and kinetic, were obtained by the first calculation method proposed previously. Figure 1 shows the experimental values of the material's complex viscosity and those predicted by applying the Arrhenius model for the two heating rates used.

Table I summarizes the resol resin's curing parameters calculated by applying Arrhenius model and the quality of the fits obtained (R^2 and MPE). The average flow activation energies (ΔE_η) calculated were 65.8 and 55.7 kJ/mol for the programmed ramps tested. In addition, the curing activation energies ($-\Delta E_k$) obtained for the resin curing process were 28.3 and 27.4 kJ/mol.

The activation energy values of the resin's viscous flow depend on the heating rate applied to the sample. In order to determine if this dependence was due either to the curing degree and/or temperature profiles across the resin sample, or to the first calculation procedure proposed, a second methodology was suggested. The flow parameters of the material were obtained in a separate way by applying the Andrade equation to data of resol resin's complex viscosity during the first stage, as described

TABLE I
Flow and Kinetic Parameters of the Resol Resin Curing Obtained by Applying the Arrhenius Rheokinetic Model (First Method)

Sample	ΔE_η (kJ/mol)	$Ln(\eta_\infty)$	$-\Delta E_k$ (kJ/mol)	$Ln(k_\infty)$	R^2	MPE[a]
Heating rate: 1°C/min						
1	71.0	−19.01	23.9	1.86	0.994	0.705
2	64.8	−17.97	30.0	4.03	0.983	0.812
3	60.3	−15.46	30.2	4.13	0.815	2.047
4	53.0	−12.51	35.5	5.67	0.921	2.139
5	79.8	−22.96	21.9	1.27	0.980	1.742
Average	65.8	−17.60	28.3	3.39	0.939	1.489
Heating rate: 5°C/min						
1	59.4	−13.17	25.6	3.23	0.977	0.410
2	55.1	−11.33	27.7	3.86	0.926	1.017
3	53.0	−9.49	27.8	3.73	0.990	1.135
4	61.3	−13.89	24.1	2.77	0.923	1.621
5	49.8	−8.15	31.7	4.90	0.964	1.071
Average	55.7	−11.20	27.4	3.70	0.956	1.051

[a] Mean prediction error. $\text{MPE} = 1/N \sum_n \frac{|r_n - y_n|}{r_n} \times 100$. N, y_n, and r_n are the number of observations, model estimation and real value, respectively.

previously. No curing reaction takes place in this stage; therefore, no overlapping occurred. Thus, the method proposed avoids the compensation effect between flow and kinetic parameters, allows separation between flow (thermal-softening stage) and curing effects, and avoids underestimation of the kinetic activation energy determined for the resin curing process.

The experimental values of the resin's complex viscosity and those predicted by applying the Arrhenius model through the second calculation procedure are shown in Figure 1.

The correlation coefficients as well as the MPE values (Table II) attained in all cases reveal an acceptable model fit to the data within the flow and curing stages (stages I and III). However, the overlapping stage (stage II) shows decreased model accuracy, which is attributed to the lack of flexibility in the rheokinetic model when it is applied through the second methodology to the stage II process. Therefore, a drawback of the second method was the decreasing quality of the obtained global fits, as the lower values of R^2 and higher MPE shown in Table II confirm when compared with those exhibited in Table I. The main advantage of this method, independent of the flow and kinetic terms, is that no differences in the values of ΔE_η and $-\Delta E_k$ were seen with respect to those attained via use of first calculation method (Table II). Thus, the second method, proposed in a previous work (due to the compensation effect found), and the dependence of the process activation energies on the heating rate for the same resin analyzed under shear strain,[19] resolved similar results to those from the first method when

TABLE II
Flow and Kinetic Parameters of the Resol Resin Curing Obtained by Applying the Arrhenius Rheokinetic Model (Second Method)

| Sample	ΔE_η (kJ/mol)	$Ln(\eta_\infty)$	R^2	$-\Delta E_k$ (kJ/mol)	$Ln(k_\infty)$	R^2	MPE[a]
Heating rate: 1°C/min							
1	66.0 ± 0.1	−16.63 ± 0.05	0.999	29.1	3.53	0.939	1.261
2	64.4 ± 0.1	−15.82 ± 0.05	0.999	28.1	3.16	0.921	1.271
3	80.6 ± 0.3	−24.28 ± 0.10	0.999	26.2	2.87	0.815	2.121
4	74.6 ± 0.3	−20.97 ± 0.13	0.998	19.8	0.35	0.921	3.487
5	68.1 ± 0.2	−17.84 ± 0.08	0.999	28.8	3.44	0.960	1.211
Average	70.7 ± 0.2	−19.11 ± 0.08	0.999	26.4	2.67	0.911	1.870
Heating rate: 5°C/min							
1	47.0 ± 0.1	−6.25 ± 0.02	0.999	25.0	3.12	0.962	0.764
2	50.6 ± 0.2	−7.86 ± 0.12	0.999	24.7	3.00	0.943	1.372
3	52.3 ± 0.3	−9.01 ± 0.10	0.999	30.7	4.59	0.973	1.387
4	61.8 ± 0.3	−13.88 ± 0.11	0.999	26.0	3.38	0.923	1.886
5	52.0 ± 0.4	−8.86 ± 0.14	0.999	31.9	4.96	0.959	1.369
Average	52.7 ± 0.3	−9.17 ± 0.10	0.999	27.7	3.81	0.910	1.356

[a] Mean prediction error.
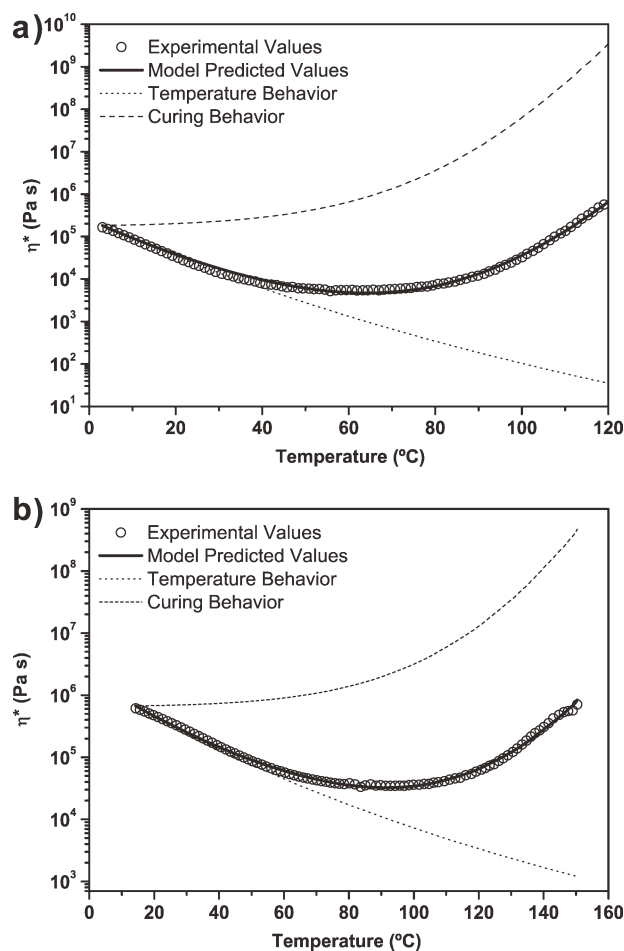
Figure 2 Experimental and predicted values of the resin's complex viscosity . Flow and curing terms contribution to the Arrhenius 6p rheokinetic model for the resol resin: (a) 1°C/min, (b) 5°C/min.

the material was studied by rectangular torsion. Uniform heating across the sample was found as the curing kinetic parameters obtained for the heating ramps employed proved, and therefore, nonthermal diffusion occurred during the experimental procedure. Similar results were found for the flow and curing parameters of the same resol resin calculated for lower heating rates (0.5°C/min).[19] Therefore, the robustness of the second method was proved due to the rheokinetic parameters of the resin's curing process do not be affected by the heating ramps employed in this work that is in agreement with parameters calculated under different heating ramps used in the literature, where the same values of kinetic parameters of the resin curing process are attained at different heating rates.[19]

Once it was proved that nonthermal diffusion occurred during the experimental procedure, the cause of the slight differences found for the flow activation energy calculated by the Arrhenius model was related to the small differences in the initial

degree-of-cure of resin due to the fixed precuring process used to reach its gelation. However, the values of flow activation energy obtained for the resol resin curing (Table I) by applying the Arrhenius model show a good agreement with those determined by Mourant et al.,[32] for the curing of a phenolic-formaldehyde-pyrolytic oil resin (31.3–77.0 kJ/mol). Lower activation energies of the viscous flow were found for thermosetting materials such as an uncured polyurethane (23 kJ/mol),[33] and an epoxy resin near its gel point (40 kJ/mol).[34] In addition, the values for flow activation energies calculated are in agreement with those determined for this material when studied under shear strain (67.1–58.3 kJ/mol).[35] The resol resin showed higher ΔE_η values than those of the other materials, because the resol resin was precured to gelation, which increases its crosslinking density and raises the flow activation energy with respect to that of uncured material.[34] The kinetic activation energies determined for the resol resin curing process (Table II) were lower than those obtained for the curing of the same material by DSC (70.7–89.0 kJ/mol),[20,25] and by isothermal rheological techniques (70.4–88.1 kJ/mol).[35,36]

The six-parameter Arrhenius model was selected as an improved model capable of increasing the quality of the data fits for the resin's complex viscosity, as shown in Figure 2.

The $-\Delta E_k$ value obtained for the resin crosslinking process was 37.2 kJ/mol, as shown in Table III. The increased value due to the change entanglement parameter (ϕ) is related to the high curing degree of the starting resin and, therefore this parameter should be considered when modeling the resin's complex viscosity evolution. The $-\Delta E_k$ is in

TABLE III
Kinetic Parameters of the Resol Resin Curing Obtained by Applying the Six-Parameter Arrhenius Rheokinetic Model

Sample	$-\Delta E_k$ (kJ/mol)	Ln (η_∞)	ϕ	n	R^2	MPE[a]
Heating rate: 1°C/min						
1	39.2	7.13	1.3	1.13	0.997	1.047
2	37.0	6.34	1.3	1.12	0.997	1.054
3	37.4	6.93	1.3	1.11	0.995	1.148
4	36.2	6.22	1.4	1.11	0.998	1.066
5	36.1	6.00	1.3	1.10	0.994	1.405
Average	37.2	6.52	1.3	1.11	0.996	1.144
Heating rate: 5°C/min						
1	36.7	6.31	1.3	1.11	0.991	0.437
2	32.2	5.41	1.3	1.09	0.998	1.245
3	40.4	7.74	1.3	1.16	0.990	0.836
4	40.2	8.10	1.3	1.17	0.985	1.782
5	40.5	7.67	1.3	1.15	0.996	0.795
Average	38.0	7.05	1.3	1.14	0.992	1.019

[a] Mean prediction error.

agreement with the values found in literature for the resol resin curing by a TMA technique and when applying the Castro-Makosco model (43.9 kJ/mol),[37] and for other resins such as a vinyl ester resin (34.0–49.0 kJ/mol),[38] and an epoxy resin (38.1–71.1 kJ/mol).[11] The chain entanglement parameter (ϕ) is in the range found for an epoxy resin curing ($1 \leq \phi \leq 2$) by Dusi and May.[26] The reaction order determined in this work for resin curing kinetics was 1.1, which is different than the most common order (unity) found in literature for the same material.[25] The calculated regression coefficients (R^2) and MPE values for six-parameter Arrhenius model were higher and lower, respectively, than those calculated by the four-parameter Arrhenius model. Therefore, to predict the rheological behavior of resins during their curing processes, the six-parameter Arrhenius model is more suitable according to the statistical parameters calculated for the performed fits.

The contribution of the thermal softening and curing process (terms of the Arrhenius model) to predict the resin's complex viscosity is represented in Figure 2. Viscous profiles of the resin were displaced in Figure 2 in order to compare both terms of Arrhenius model in the same stage.

An increase in the activation energy for the viscous flow of resin would provide higher values of this term, which reveals that the lower limit temperature is higher for this curing stage of the resin's complex viscosity profile. Therefore, higher curing activation energies would be achieved via the application of the six-parameter Arrhenius model to viscosity data for resin curing, which would increase the agreement between dynamic and isothermal rheokinetic parameters for the material crosslinking process.

CONCLUSIONS

The rheological behavior of a resol resin curing during dynamic temperature analysis reveals three different stages: a viscous flow stage, an overlapping stage and a curing stage. The temperature range of these stages depends on the heating rate used.

Two calculation methods have been proposed in order to obtain the viscous flow and the curing kinetic parameters of the material using the four- and six-parameter Arrhenius rheokinetic models. There were no differences between the models observed when applying either methodology. The six-parameter Arrhenius model is suggested as the best rheokinetic model to describe the resin's behavior during its cure under dynamic operating conditions by rheometry based on rectangular torsion strain. The activation energy obtained for resol resin curing was ~ 38.0 kJ/mol for both 1 and 5°C/min heating rates. These values are in agreement with mechanical

activation energy found in the literature for the material studied.

The highest heating rate used, 5°C/min, was best operating condition for obtaining the rheological profile of the resol resin curing during dynamic temperature tests. This superior performance was due to the lower operating time and wider temperature and curing degree ranges studied. Finally, this work has shown that no degradation process takes place during the resin curing.

References

1. Gardziella, A.; Pilato, L.; Knop, A. Phenolic Resins; Springer: New York, 2000.
2. Halley, P. J.; Mackay, M. E. Polym Eng Sci 1996, 36, 593.
3. Kim, J. T.; Martin, D.; Halley, P.; Kim, D. S. Compos Interfaces 2007, 14, 449.
4. Martin, G. C.; Tungare, A. V.; Gotro, J. T. Polym Eng Sci 1989, 29, 1279.
5. Roller, M. B. Polym Eng Sci 1986, 26, 432.
6. Wang, J.; Laborie, M. P. G.; Wolcott, M. P. Thermochim Acta 2007, 465, 18.
7. Knop, A.; Pilato, L. Phenolic Resins; Springer: Berlin, 1995.
8. Pascault, J. P.; Sautereau, H.; Verdu, J.; Williams, R. J. J. Thermosetting Polymers; Marcel Dekker, 2002.
9. Sperling, L. H. Introduction to Physical Polymer Science; Wiley: New Jersey, 1992.
10. Klucákova, M. Compos Sci Technol 2004, 64, 1041.
11. Laza, J. M.; Julian, C. A.; Larrauri, E.; Rodríguez, M.; León, L. M. Polymer 1999, 40, 35.
12. Peng, W.; Riedl, B. Polymer 1994, 35, 1280.
13. Castro, J. M.; Macosko, C. W. Soc Plast Eng 1980, 26, 434.
14. Cai, H.; Li, P.; Sui, G.; Yu, Y.; Li, G.; Yang, X.; Ryu, S. Thermochim Acta 2008, 473, 101.
15. Harsch, M.; Karger-Kocsis, J.; Holst, M. Eur Polym J 2007, 43, 1168.
16. Kiuna, N.; Lawrence, C. J.; Fontana, Q. P. V.; Lee, P. D.; Selerland, T.; Spelt, P. D. M. Compos Part A-Appl Sci Manuf 2002, 33, 1497.
17. Gillham, J. K. J Appl Polym Sci 1986, 26, 1429.
18. Prime, R. B. Thermal Characterization of Polymeric Materials; Turi, A. Ed., Academic Press: San Diego, 1997, p 435–568.
19. Domínguez, J. C.; Alonso, M. V.; Oliet, M.; Rojo, E.; Rodríguez, F. Eur Polym J 2010, 46, 1237.
20. Alonso, M. V.; Oliet, M.; García, J.; Rodríguez, F.; Echeverría, J. Chem Eng J 2006, 122, 159.
21. Broyer, E.; Macosko, C. W. AIChE J 1976, 22, 268.
22. Hargis, M.; Grady, B. P.; Aktas, L.; Bomireddy, K. R.; Howsman, S.; Altan, M. C.; Rose, T.; Rose, H. J Compos Mater 2006, 40, 873.
23. Lin, S. P.; Shen, J. H.; Han, J. L.; Lee, Y. J.; Liao, K. H.; Yeh, J. T.; Chang, F. C.; Hsieh, K. H. Compos Sci Technol 2008, 68, 709.
24. Alonso, M. V.; Oliet, M.; Domínguez, J. C.; Rodríguez, F. 10th European Workshop on Lignocellulosics and Pulp (EWLP), Stockholm, 2008.
25. Alonso, M. V.; Oliet, M.; Pérez, J. M.; Rodríguez, F.; Echeverría, J. Thermochim Acta 2004, 419, 161.
26. Dusi, M. R.; May, C. A.; Seferis, J. C. ACS Symposium Series 1983, 227, p 300–316.
27. Kenny, J. M.; Apicella, A.; Nicolais, L. Polym Eng Sci 1989, 29, 973.
28. Hatakeyama, T.; Quinn, F. X. Thermal Analysis Fundamental and Applications to Polymer Science; Wiley: West Sussex, 1999.

29. Menard, K. P. Dynamical Mechanical Analysis. A Practical Introduction; CRC, 1999.
30. Ryan, M. E. Polym Eng Sci 1984, 24, 698.
31. Simpson, J. O.; Bidstrup, S. A. J Polym Sci Part B: Polym Phys 1995, 33, 55.
32. Mourant, D.; Riedl, B.; Rodrigue, D.; Yang, D. Q.; Roy, C. J Appl Polym Sci 2007, 106, 1087.
33. Dimier, F.; Sbirrazzuoli, N.; Vergnes, B.; Vincent, M. Polym Eng Sci 2004, 44, 518.
34. Kamal, M. R. Polym Eng Sci 1974, 14, 231.
35. Domínguez, J. C.; Alonso, M. V.; Oliet, M.; Rodríguez, F. Eur Polym J 2010, 46, 50.
36. Domínguez, J. C.; Oliet, M.; Alonso, M. V.; Rojo, E.; Rodríguez, F. J Appl Polym Sci 2011, doi: 10.1002/app.34713.
37. Alonso, M. V.; Oliet, M.; Pérez, J. M.; Rodríguez, F. 9th European Symposium on Thermal Analysis and Calorimetry, Krakow, 2006.
38. Martin, J. S.; Laza, J. M.; Morrás, M. L.; Rodríguez, M.; León, L. M. Polymer 2000, 41, 4203.