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Chemorheological analysis of a gelled resol resin curing under non-isothermal conditions by shear strain

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ABSTRACT

The chemorheological behavior of curing of a resol resin was analyzed under non-isothermal conditions beyond the gelation point. Two heating ramps (0.5 and 1 °C/min) from 0 to 100 °C were performed. The rheological measurements of the resin were performed using oscillatory shear strain. The obtained profiles for the resin's complex viscosity were applied, after treatment by two calculation methods, to the four- and six-parameter Arrhenius models. These models allow one to establish the viscous flow region of the resin and the kinetic parameters of the material's curing process. The six-parameter Arrhenius model was selected as the best method for modeling of the resin's rheological behavior during its curing process. The viscous-flow activation energies determined for the gelled resol resin curing were 67.1 and 58.3 kJ/mol for the 0.5 and 1 °C/min heating rates, respectively. The activation energies of the resin curing process were 41.7 and 67.0 kJ/mol for each temperature ramp.

1. Introduction

Phenol–formaldehyde resins are the oldest thermoreactive oligomers used in the plastics industry to produce items by forming a relatively low viscosity melt that subsequently transition into a cured material [1]. These resins have been applied in many commercial uses such as thermal and sound insulation, molding compounds, foundry resins and composite wood material [2]. Their multiple applications are due to the favorable properties of the resins, including excellent thermal stability, fire and chemical resistances and their rapid and easy crosslinking [3]. The fluidity of the resin and its curing rate are key properties for obtaining high-quality products. The rheological behavior of the resin curing determines the technical properties of the final material [1].

Due to the complexity of the system, the kinetics of resol resin curing is determined by a set of simultaneous reactions. Despite this, resin curing kinetics is perceived commonly as a single-state reaction described by one kinetic model. This assumption enables the relation of the material's viscosity change over time to its curing kinetics [1]. The study of viscoelastic behavior in reacting systems is called chemorheology [4]. The chemoviscosity of thermosetting resins during curing is affected by several variables including temperature, pressure, shear rate, time and the filler's properties. Commonly, each one of the variables is examined by separate tests. Curing's influences on a material are analyzed according to the temperature and time effects on the resin's complex viscosity. Thermal effects must be considered during the heating ramp, both while heating to reach the operating temperature for isothermal analysis and while performing non-isothermal curing tests.

Two main transformations, gelation and vitrification, take place during the formation of a polymer network. Gelation corresponds to the incipient formation of an infinite network; from a rheological point of view, this is defined as the irreversible transformation of the sample from a viscous liquid to an elastic solid. Vitrification involves the resin transformation from a liquid to a glassy state [5].

The curing processes of phenolic resins have been widely studied, especially by thermal analysis techniques [6–10]. Rheological analyses of resin crosslinking have been studied

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mostly under isothermal operating conditions [11]. Non-isothermal rheological analysis provides, in a single run, the viscous flow and kinetic parameters for the resin curing and thus avoids the inconvenience of a multiple-test analysis needed for isothermal studies. Dynamic temperature rheological analysis offers a quantitative view of the adhesion mechanics from which the glass transition, gelation, and vitrification points may be inferred [12].

In this study, complex viscosity data were obtained on a gelled resol resin under dynamic temperature parallel-plate testing at high conversion, when the chain length slows the rate of polymerization as the monomer content is extinguished. The profiles obtained were analyzed by the four- and six-parameter Arrhenius chemorheological model [13,14]. Two calculation methodologies are proposed in order to obtain the flow and kinetic parameters of the resol resin curing. The results obtained are compared with the thermal analysis and isothermal rheological curing kinetics of the resol resin obtained in previous works [9,11,15].

2. Experimental

2.1. Materials

The resol resin was supplied by Hexion Specialty Chemicals Ibérica S.A. The main properties of resin were: free phenol content (<0.2%), viscosity (25 °C, 275–475 cP) and a solids content range of 45–47%. The gel time of the resin at 130 °C was between 9 and 10 min, in accordance with ISO B9396 B.

2.2. Sample preparation

The preparation of the starting resol resin was based on a precuring process by hot-pressing in a laboratory platen press (Collin® P300P). The obtained resin reached a degree of cure that corresponds to the material's gel point ($\alpha_{gel} = 0.65$) [9]. The precuring procedure was previously adopted for the isothermal analysis of the resol resin [11].

2.3. Rheological runs

Rheological runs were performed using an ARES Rheometer (TA Instruments®) with a 25 mm upper plate and a 42 mm lower parallel plate. The lower plate was filled for sample immersion in a silicon surrounding fluid (Dow Corning 200® FLUID 100 cSt) to avoid drying of the material surface. The autotension rheometer option was enabled to prevent contact loss between the sample and the plates. An axial force of 100 g was applied to the sample and was kept constant during the rheological tests. The frequency was fixed at 1 Hz, and two heating ramps, 0.5 and 1 °C/min, were carried out from 0 to 100 °C. The resol resin samples were analyzed by a strain sweep from 0.01 to 1% at 60 °C and 1 Hz to confirm that the linear viscoelastic region of the cured resol resin (LVR) was never exceeded during rheological testing.

2.4. Chemorheological models

Chemorheological models were developed, classified and suggested according to the variables studied (e.g., viscosity or complex viscosity was measured for steady or dynamic rheological measurements, respectively) [4,14]. In this work, the Arrhenius model, the predominant empirical model [16], was proposed to describe the change in the resin's complex viscosity due to thermal level increase, the resin curing process and a combination of both phenomena. The relation between viscosity (η) and complex viscosity (η^*) of the material was assumed to be according to the Cox–Merz rule. Therefore, the resol's complex viscosity evolution was followed by applying the Arrhenius rheokinetic model [17]. The four-parameter Arrhenius model is described by

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

where η^* is the resin's complex viscosity at absolute temperature T, $\eta_0{}^*$ is the flow constant, and $k(T)$ is the kinetic constant of the curing process at a given temperature T.

The Arrhenius chemorheological model is composed of two terms. In the first term, the resin's viscous flow is described using the Andrade expression, as shown in Eq. (2). The second term represents the resin's curing kinetics and describes the complex viscosity increase due to increasing molecular weight of the material during its polymerization (Eq. (3)):

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

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

where $\eta_\infty{}^*$ is the reference complex viscosity at "infinite temperature", ΔE_η is the Arrhenius activation energy for resin's complex viscosity, t is the curing time, R is the universal gas constant, k_∞ is the kinetic constant of process (analogous to $\eta_\infty{}^*$) and $-\Delta E_k$ is the kinetic activation energy (analogous to ΔE_η).

A proportionality factor (ϕ) proposed by Keenan et al. [13], which is suggested to relate the amount of chain entanglement with the rheological behavior of the resin during its crosslinking, was introduced into the Arrhenius model. This model was improved to include the reaction order so as to reduce the limitations revealed in some cases for the fitting of a resin's viscosity data to the applied model. The six-parameter Arrhenius chemorheological model is described by Eq. (4):

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

We propose two calculation methods to apply the four- and six-parameter Arrhenius models to data on the resin's complex viscosity to describe the evolution of viscosity during the curing process:

- Method 1: Viscous flow and curing parameters of the Arrhenius model were calculated simultaneously by a least squares sum 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. The resin curing parameters provided by the Arrhenius model, $-\Delta E_k$ and $\ln(k_\infty)$, were obtained by applying the kinetic model to the complete profile measured for the resin's complex viscosity *vs.* temperature using a least squares sum algorithm and the flow parameters previously calculated.

3. Results and discussion

The evolution of the material's complex viscosity during the non-isothermal rheological runs is shown in Fig. 1. The highest operating temperature was fixed at 100 °C because the water content of the resin causes dispersion in the resin's complex viscosity measurements, even after being pre-cured beyond its gel point. The small amount of free surface of the parallel plate geometry is the main reason that dispersion takes place when operating at temperatures over 100 °C. This phenomenon has been observed in isothermal mode experiments reported in the literature [11,18].

The complex viscosity of the resin decreases due to the thermal effects (stage I), as shown in Fig. 1. The decreasing rate depends on the flow activation energy of the material during this first stage. The temperature range for this stage, as well as that of stages II and III, depends on the heating rate. As the operating temperature increases, the resin curing process starts, and the decrease in viscosity is compensated by the viscosity increase due to resin crosslinking [4,19,20]. A second stage, where thermal softening and curing phenomena overlap, was found. A minimum value of the material's complex viscosity was obtained when operating at 0.5 °C/min (60 °C). When a 1 °C/min heating ramp was employed, the minimum temperature becomes a plateau region from 55 to 70 °C. This minimum complex viscosity is a key value because, at these conditions, the trapped bubbles in the resin are released. In these conditions, the resin is highly mobile, and the viscous flow forces are sufficiently large to overcome the surface tension forces that trap the bubbles [21]. The temperature at which the minimum value of the resin's complex viscosity is reached depends on the heating ramp. The displacement of the minimum value to higher temperatures as the heating rate increases has been widely reported for thermal analysis techniques [22–24]. Finally, for both heating rates employed in this study, a curing stage that controls the kinetics of the overall process was found until the top operating temperature was attained. A linear behavior of the resin's complex viscosity was found during this stage. Thus, the rate of the material's curing process was reaction-controlled, and diffusion effects on the kinetics of the overall curing process were not found, as occurred for the isothermal analysis in a previous work [11]. The narrow temperature range of the third stage for the 1 °C/min heating rate implies a significantly lower number of rheological measurements than the corresponding values obtained when operating with a 0.5 °C/min heating ramp.

The resol resin was pre-cured beyond gelation, and a resin curing degree of 0.65 was reached, as reported in a previous work [25]. The curing's overall rate is controlled by the crosslinking reaction during the operating time for all of the resin samples. Thus, the heating rates applied to the resol samples are high enough to avoid the control of overall process kinetics by diffusion. This was confirmed by the absence of non-linear behavior in the complex viscosity logarithm as the resin's degree of cure approaches the vitrification point at each temperature during the rheological runs.

The four-parameter Arrhenius chemorheological model, Eq. (1), was applied to the resol resin's complex viscosity data for the two heating rates tested, 0.5 and 1 °C/min. The experimental values of the resin's complex viscosity and those predicted by the rheokinetic model are compared in Fig. 2.

The kinetic parameters of the resol resin's curing process, as calculated by the Arrhenius model for the two heating rates studied, are exhibited in Table 1. The average

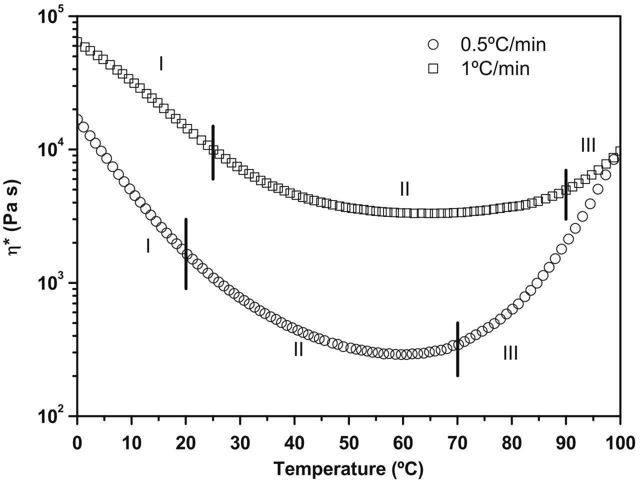

Fig. 1. Resol resin's complex viscosity behavior *vs.* temperature for the programmed heating ramps: 0.5 and 1 °C/min.

flow activation energies (ΔE_η) were 76.4 and 85.7 kJ/mol, and the curing activation energies (ΔE_k) were 25.3 and 14.1 kJ/mol for 0.5 and 1 °C/min, respectively. The viscous-flow activation energies calculated were within the range obtained by Mourant et al. [26] for a phenolic-formaldehyde-pyrolytic oil resin (31.3–77.0 kJ/mol). Nevertheless, these values were higher than those found in the literature for resol resins and other thermosetting materials such as a polyurethane (23 kJ/mol) and an epoxy resin (40 kJ/mol) [27,28]. The viscous-flow activation energy of a material increases as its rheological behavior approaches that of an ideal solid. The resol resin studied was gelled, which potentially explains the high viscous-flow activation energies attained with respect to other uncrosslinked polymers.

The activation energies for viscous flow and for the curing process of the material depend on the heating rate applied to the sample, a phenomenon confirmed by the differences found for both values (Table 1). These differences could be explained as due to the curing degree and/or to the temperature profiles across the resin sample, which are highly related to the heating rate applied. In addition, the first calculation procedure proposed could be one of the causes of the differences found. The second calculation method is proposed to obtain the material's flow and kinetic parameters during the curing process and to reveal if the cause of any heating rate dependence is due to the calculation method employed. This calculation method avoids the compensation effect between the flow and kinetic parameters of the model, because the

Table 1
Viscous flow and kinetic parameters of resol resin curing process obtained by the four-parameter Arrhenius chemorheological model (1st method).

Sample	$-\Delta E_\eta$ (kJ/mol)	$\mathrm{Ln}(\eta_\infty)$	$-\Delta E_k$ (kJ/mol)	$\mathrm{Ln}(k_\infty)$	R^2
Heating rate: 0.5 °C/min					
1	83.5	−27.13	26.0	2.25	0.994
2	78.3	−23.22	19.2	−0.32	0.949
3	72.1	−21.95	25.7	2.02	0.995
4	72.5	−21.46	24.7	1.56	0.995
5	75.8	−23.75	30.9	3.90	0.998
Average	76.4	−23.50	25.3	1.88	0.986
Heating rate: 1 °C/min					
1	78.2	−22.79	13.6	−1.75	0.988
2	83.5	−25.68	11.1	−2.60	0.993
3	89.7	−28.62	12.1	−2.10	0.987
4	89.3	−28.65	15.2	−0.97	0.998
5	87.7	−27.25	18.4	0.09	0.998
Average	85.7	−26.60	14.1	−1.47	0.993

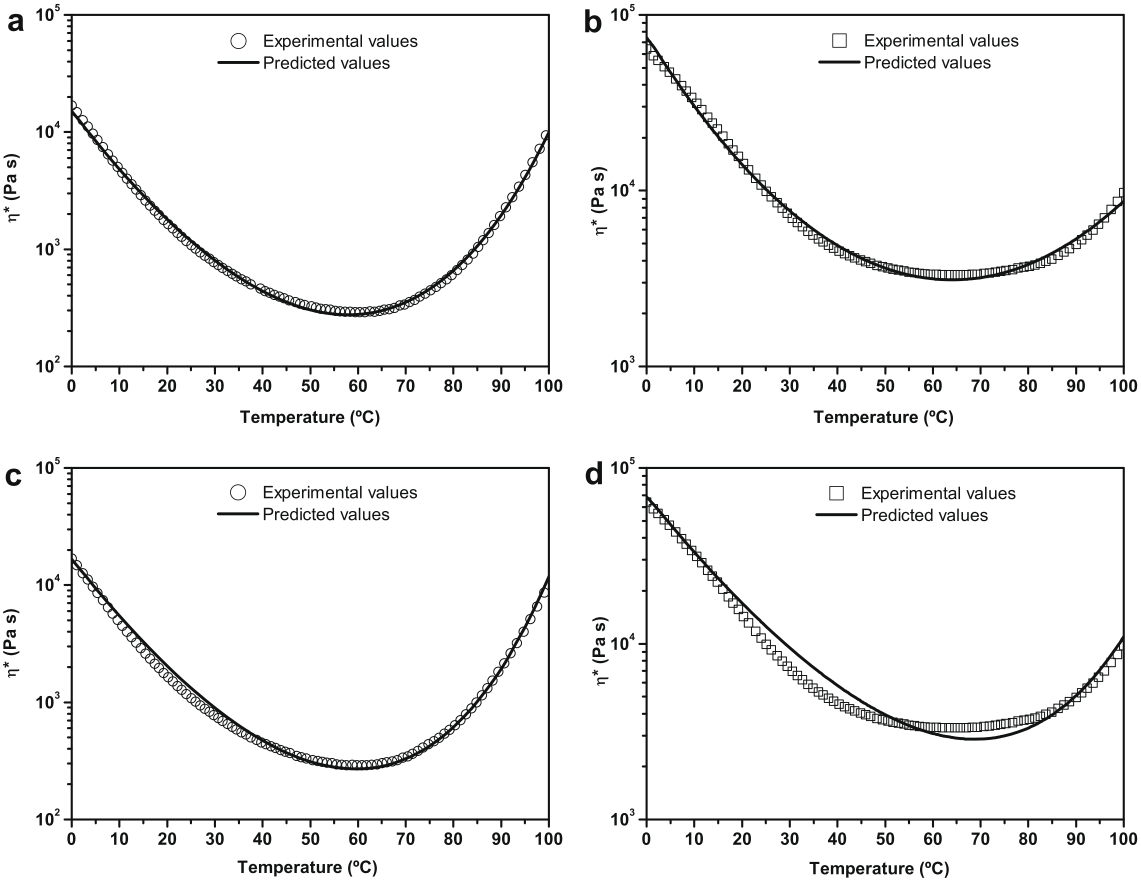

Fig. 2. Experimental values of resin's complex viscosity and those predicted by applying the four-parameter Arrhenius model *vs.* temperature. 1st method: (a) 0.5 °C/min, (b) 1 °C/min; 2nd method: (c) 0.5 °C/min, (d) 1 °C/min.

viscous flow parameters of the resin are obtained separately. The resin's complex viscosity and the Arrhenius model's predicted values obtained by the second procedure proposed are shown in Fig. 2.

Excellent fits ($R^2 = 0.999$) of the flow region data to the model were found, largely due to the separate fitting procedure for this stage. However, the overlapping region showed a decreasing accuracy of the model, which was attributed to the lack of flexibility for the application of these data to a chemorheological model by the second methodology proposed. Therefore, a drawback when dealing with this calculation method was the decreasing quality of the obtained global fits with respect to the first method, as shown in Table 2. Nevertheless, a great advantage was obtained by applying this second methodology, which is independent of the heating rate employed, to establish the viscous flow and kinetic parameters of the curing process described by the model for the resin. These results are shown in Table 2. The viscous-flow activation energies obtained for the resol resin were 67.1 and 58.3 kJ/mol for 0.5 and 1 °C/min, respectively. These values were lower than those obtained previously by the Arrhenius model when the first calculation method was applied. This discrepancy points to the existence of the aforementioned compensation effect. In Table 2, the agreement between the values of the kinetic activation energies calculated for both stages of the resol resin's curing confirms this point. Thus, the second method avoids the compensation effect between the viscous flow and the kinetic parameters of the resol curing process, and it therefore allows the possibility of different couples of terms to reasonably describe the same profile for the resin's complex viscosity. The flow activation energies attained remained within the values obtained by Mourant et al. [26] for a phenolic-formaldehyde-pyrolytic oil resin.

The kinetic activation energies determined for the resol resin curing process (ca. 33.1 kJ/mol) were lower than those obtained for the same material by DSC (70.7–89.0 kJ/mol) and shear strain rheological analysis under isothermal conditions (88.1 kJ/mol) [9,11,25]. The accuracy of the fits decreased in this case with respect to the four-parameter Arrhenius model applied under the first calcula-

Table 2
Viscous flow and kinetic parameters of resol resin curing process obtained by the four-parameter Arrhenius chemorheological model (2nd method).

Sample	$-\Delta E_\eta$ (kJ/mol)	Ln(η_∞)	R^2	$-\Delta E_k$ (kJ/mol)	Ln(k_∞)	R^2
Heating rate: 0.5 °C/min						
1	78.1 ± 0.2	−24.69 ± 0.07	1.000	30.9	3.91	0.994
2	60.0 ± 0.2	−15.24 ± 0.08	0.999	32.5	4.08	0.962
3	65.9 ± 0.1	−19.13 ± 0.01	1.000	32.0	4.14	0.992
4	63.7 ± 0.2	−17.55 ± 0.09	0.999	32.9	4.34	0.991
5	67.6 ± 0.2	−20.17 ± 0.06	1.000	38.5	6.44	0.968
Average	67.1 ± 0.2	−19.36 ± 0.06	1.000	33.4	4.58	0.981
Heating rate: 1 °C/min						
1	47.0 ± 0.1	−12.58 ± 0.11	1.000	31.4	4.09	0.904
2	50.6 ± 0.2	−10.74 ± 0.14	0.998	34.3	5.01	0.994
3	52.3 ± 0.3	−16.57 ± 0.05	1.000	28.4	3.24	0.992
4	61.8 ± 0.3	−16.62 ± 0.16	0.998	32.8	4.82	0.959
5	52.0 ± 0.4	−16.23 ± 0.20	0.998	38.5	6.75	0.972
Average	52.7 ± 0.3	−14.55 ± 0.13	0.999	33.1	4.78	0.964

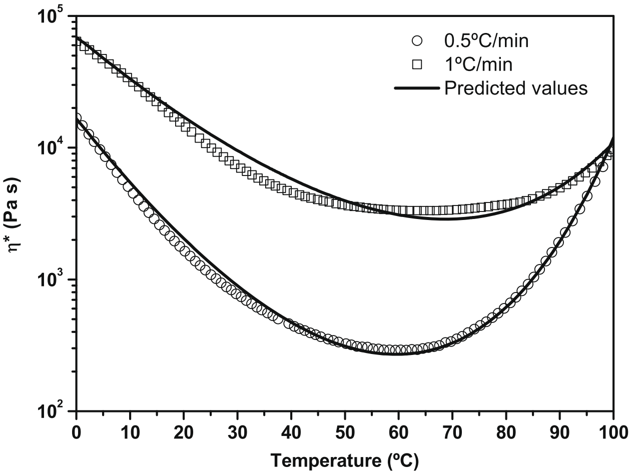

Fig. 3. Experimental values of resin's complex viscosity and those predicted by applying the six-parameter Arrhenius model *vs.* temperature. 2nd method: 0.5 and 1 °C/min.

tion method proposed, especially for the 1 °C/min heating ramp. The six-parameter Arrhenius model was selected as an improved model capable of increasing the quality of the fits achieved for the data of the resin's complex viscosity during its curing, as shown in Fig. 3.

The average activation energies attained for the resin curing process were 41.7 and 67.0 kJ/mol for 0.5 and 1 °C/min heating ramps, respectively, as shown in Table 3. The $-\Delta E_k$ obtained using the lower heating rate was in agreement with the value found in the literature for the resol resin curing process studied under a mechanical technique, such as thermomechanical analysis (TMA), when applying the Makosco model (43.9 kJ/mol) [15,29]. This value is in agreement with the activation energies obtained for other thermosetting materials such as a polyurethane resin (43.6 kJ/mol) [27], epoxy resins (25.5–71.1 kJ/mol) [30,31], and an epoxy/amine resin (51.3 kJ/mol) [32]. The activation energy of the resin crosslinking process obtained with a temperature ramp of 1 °C/min (67.0 kJ/mol) was significantly higher than that attained with 0.5 °C/min, and this value is close to the kinetic energy of the resol curing process determined under isothermal conditions by torsion strain of the same material (70.4 kJ/mol) [33] and by DSC (70.7 and 74.2 kJ/mol) [9,25]. Nevertheless, an increasing lack of fit ($R^2 = 0.985$) and a disagreement between experimental and predicted values of the resin's complex viscosity was found for the curing stage during the 1 °C/min heating ramp, as shown in Fig. 3. In addition, the resin curing reaction stage provided by the 1 °C/min temperature ramp presented a narrow temperature range. These facts suggest that the value obtained for the activation energy, while using a 1 °C/min ramp, must be discarded. The 0.5 °C/min heating rate is proposed for use as the best operating conditions in order to determine the rheological behavior of the resol resin during its curing process. The chain entanglement parameter obtained ($\phi = 1.2$) was in the range found for an epoxy resin ($1 \leqslant \phi \leqslant 2$) by Dusi and May [34], and the reaction order ($n = 1.13$) was close to the most common value (unity) found for the resol resin curing process [9].

The differences found for the $-\Delta E_k$ values of resin curing by dynamic rheological tests and isothermal rheological studies by shear strain could be explained by the overlapping of the viscous flow stage and the curing reaction during the dynamic runs. In addition, the increasing ΔE_η as the crosslinking process advances was not considered by either the four- or six-parameter Arrhenius model.

Table 3
Kinetic parameters of the resol resin curing process obtained by the six-parameter Arrhenius rheokinetic model.

Sample	$-\Delta E_k$ (kJ/mol)	Ln(η_∞)	ϕ	n	R^2
Heating rate: 0.5 °C/min					
1	35.6	5.38	1.5	1.09	0.988
2	47.8	9.86	1.2	1.28	0.996
3	38.4	6.51	1.2	1.10	0.993
4	40.0	6.56	1.2	1.11	0.997
5	46.9	9.75	1.0	1.09	0.999
Average	41.7	7.61	1.2	1.13	0.995
Heating rate: 1 °C/min					
1	66.2	17.47	1.2	1.85	0.978
2	76.0	20.66	1.5	2.34	0.997
3	59.3	14.24	1.2	1.63	0.956
4	59.7	15.13	1.2	1.51	0.998
5	73.6	19.99	1.2	1.65	0.998
Average	67.0	17.50	1.3	1.80	0.985

4. Conclusions

Three different regions were determined for the rheological behavior of the resol resin under dynamic temperature analysis: viscous flow, overlapping, and curing reaction. The temperature ranges of these regions depend on the heating rate employed, and for a 1 °C/min temperature ramp, the curing region was quite narrow.

Significant differences were found when different calculation methods were used to obtain viscous flow and curing kinetic parameters of the material through the four-parameter Arrhenius chemorheological model. The second method is suggested to be more suitable because a compensation effect does not occur between the viscous flow and the curing reaction of the resin.

The application of chemorheological data to a six-parameter Arrhenius model through the second calculation method was suggested as the best way to describe the resin's behavior during its curing under non-isothermal conditions when a 0.5 °C/min heating ramp is employed. The activation energy obtained for resol resin curing was 43.9 kJ/mol, which is in agreement with the mechanical activation energy found in the literature for the curing process of a similar material studied using other techniques. Lower heating ramps (<1 °C/min) were found to be suitable for studying the curing of this resol resin, because the temperature range is sufficiently wide for modeling the curing region of the process.

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