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Chemorheological study of the curing kinetics of a phenolic resol resin gelled

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The changes in the resin viscosity, conductivity, mass, and enthalpy during curing reactions have been studied to obtain kinetic parameters that allow modeling of the resin behavior throughout its industrial application. In this work, isothermal rheological tests of a phenolic resol resin were performed in order to study its complex viscosity during crosslinking reactions. Samples were prepared by a precuring treatment in a heated plate press to reach gel point of the resin. Rheological analyses of resol resin curing were carried out at five different temperatures (80–100 °C), and the kinetic models of Arrhenius and Kiuna were applied. The resol resin curing presented an activation energy of 72.1 kJ/mol according to the Arrhenius model. The Kiuna model was proposed to fit the non-linear evolution of the resin's complex viscosity at the highest temperatures. This kinetic model was suitable for predicting the changes in the complex viscosity of the resol resin after its gelation, and the process activation energy obtained for the second order polynomial applied in this model was 88.1 kJ/mol. In addition, the profile for the degree of curing of resol resin was determined from measurements of the material's elastic modulus.

1. Introduction

Interest in the curing kinetics of thermosetting materials is growing due to the broad number of applications that need to obtain homogeneous polymers, to develop new composite materials, to achieve adequate cures for the best application specific properties of the resin, and to attain lower costs. The curing processes of phenolic resins have been widely studied, mostly by thermal analysis techniques [1–3]. Models of resins' rheological properties during curing are a key development milestone for improving both the control over the curing process and the final product performance.

The curing of thermosetting polymers is a complex process that affects the polymer's rheological behavior due to changes in the physical properties of the material. These physical properties include the viscosity and the linear viscoelasticity complex modulus [4–6]. Chemorheology focuses on the study of these rheological property changes [7]. Gelation and vitrification, which are related to relevant changes in the rheological properties of the material, are phenomena that take place during the curing process of the resin.

The gelation stage of curing is an irreversible transformation of the sample state from a viscous liquid to an elastic solid when the resin reaches a certain degree of conversion. This phenomenon is detected by techniques based on mechanical (DMTA), electrical (DEA), and viscoelastic (rheometer) properties measurements. Gelation can be determined via the following rheological criteria: (1) the point where the elastic modulus, G', and the viscous modulus, G'', are equal and $\tan(\delta) = 1$ [8]; (2) the point at which $\tan(\delta)$ becomes independent of the frequency [9]; (3) the maximum in the $\tan(\delta)$ [10,11]; (4) the crossing point between the tangent line of the elastic modulus curve and the baseline $G' = 0$ [11]; and (5) the onset of decrease in the rate of growth of the viscous modulus during the polymer cure [12].

Vitrification is a reversible transition defined as the change from the liquid, or rubbery, state of the resin to the

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Nomenclature

α	curing degree of the resin
α'	logarithm of the reduced complex viscosity
α_{gel}	curing degree of the resin at its gel point
α_{onset}	onset degree of cure of the resin for the diffusion stage
α_v	degree of cure of the resin for vitrification transition at the operating temperature
ΔE_η	Arrhenius flow activation energy
ΔE_k	kinetic activation energy of resin curing process
δ	phase angle
η^*	complex viscosity of resol resin at absolute temperature T
η_0^*	complex viscosity of the uncured resin at temperature T
η_∞^*	reference complex viscosity of resol resin at "infinite temperature"
Γ	torque
T	elapsed cure time
DEA	dielectric analysis
DMTA	dynamic mechanical thermal analysis
DSC	dynamic scanning calorimetry
G'	elastic modulus
G''	viscous modulus
$G'(t)$	elastic modulus at time t
$G'(t_{\alpha=0})$	elastic modulus for the prepolymer
$G'(t_{\alpha=1})$	elastic modulus for the fully cured resin
$k(T)$	rate of advance of the curing process of resin at temperature T
k_∞	kinetic constant at "infinite temperature"
LVR	linear viscoelastic region
p_2	fitting parameter
PET	polyethylene terephthalate
R	universal gas constant
RSS	residual sum of squares
t	curing time
T_2	hypothetical critical temperature below which no chemical controlled reaction could occur
T_{g0}	glass-transition temperature of the uncured material
TMA	thermo mechanical analysis
TTT	time–temperature–transformation

glassy state due to an increase in the crosslinking density and molecular weight of the polymer, which may occur during the curing process [5]. The curing reactions of resin continue towards the formation of a network with a high crosslinking density. Vitrification leads to resin curing kinetics to be controlled by diffusion in the resin, and this leads to a progressive decay in the reaction rate of the process [13–16].

The degree of gelation (α_{gel}) and vitrification (α_v) in the resin during its cure at the operating temperature can be obtained by the TTT diagram of system. This is a useful tool for studying the different state transitions of thermosetting polymers during the curing process and for predicting changes in their properties [17–19].

The kinetics of resin curing depends upon several factors. The most important are the material formulation, the curing operating conditions and the technique employed to characterize the resin. The kinetics of the resol resin curing process has been studied by techniques such as DSC, DMTA, TMA and rheology [11,20–22]. Different models for the chemorheological study of the curing kinetics of thermosetting polymers have been developed. The most relevant rheokinetic models found in literature are from Castro–Makosco and Arrhenius [7,23]. The Castro–Macosko model determines the kinetics of the resin curing process through the time of gelation obtained by rheological techniques. The Arrhenius model is a first order kinetic model that predicts the evolution of the material's viscosity under either isothermal or non-isothermal curing reactions. Some authors, however, have suggested other chemorheological models for certain materials such DFC (fluoromethylene cyanate ester), lignin-based-epoxy/anhydride, and epoxy/amine resins [24–26].

Commonly, the chemical curing degree of a thermosetting polymer is analyzed by thermal analysis techniques such as DSC [14]. An aspect that is not widely dealt with in literature is the study of the resin's degree of mechanical conversion. According to different authors [11,27–29], this degree of conversion can be calculated using rheological properties of the material such as the complex modulus (G^*), the elastic modulus (G') and the resulting torque (Γ) value.

The curing process of the commercial phenolic resol resin was studied by a DSC technique in a previous work [20]. The profiles of the material's curing degree were obtained under dynamic temperature tests through several heating rates. The kinetic parameters of the resin curing were obtained by a nth order model and model-free kinetic analysis. The present study employed a new approach to the knowledge of the kinetics of the resin curing process through the analysis of the chemorheological behavior of this thermosetting polymer.

In this work, the rheological behavior of a resol resin cured under several isothermal conditions was reported in order to study the rheokinetics of its curing process. The existence of a diffusion region that controls the kinetics of the overall process was proved, and the temperature dependence of the resin curing degree at the onset of this stage was determined. The kinetic parameters of the curing were calculated from the Arrhenius and Kiuna chemorheological models. The degree of the material's mechanical conversion was calculated from the measured elastic modulus in order to determine the relationship between this conversion and the chemical degree of resin cure obtained by DSC in a previous work [20].

2. Experimental

2.1. Materials

A resol resin used as an adhesive in plywood products was supplied by Hexion Speciality 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%. Gel time of the resin at 130 °C is between 9 and 10 min, in accordance with ISO B9396 B.

2.2. Sample preparation

The preparation of the sample was based on a precuring process by hot-pressing (Collin® P300P press) in a steel mold (16 × 11 mm). The mold was coated by PET (Goodfellow® ES301230) plastic to avoid foam formation. For precuring, the time, temperature and pressure conditions were optimized to obtain a gelled resin with the required degree of cure for its rheological characterization. The resol resin was poured into a mold at 100 bar and 105 °C over 18 min.

2.3. Rheological measurements

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 sample and plates. An axial force of 100 g was applied to the sample and was kept constant during rheological tests. Frequency was fixed at 1 Hz, and resin isothermal curing runs (80, 85, 90, 95 and 100 °C) were carried out for 30 min. The initial temperature was 25 °C and a 20 °C/min heating ramp was programmed to set the operating temperature.

For each operating temperature tested, the linear viscoelastic region (LVR) of the material was determined through a strain sweep after isothermal curing. Strain sweeps were carried out at 60 °C, 1 Hz, and a strain range from 0.01 to 1% was used to ensure that the resin samples were always within the LVR.

2.4. Diffusion stage onset

The onset time for the diffusion stage (the period during which diffusion rates control the kinetics of overall resin curing process) was obtained during isothermal rheological tests at the beginning of non-linear evolution of the resin's complex viscosity. The curing degree of the resin at the onset time (α_{onset}) was obtained and related to the TTT diagram obtained by DSC and TMA techniques in a previous work [30]. The resin's cure conversion at onset was also related to curing temperature as established by Eq. (1) [13,24].

$$\alpha_{\text{onset}}(T) = p_2 \cdot \left(\frac{1}{T_2} - \frac{1}{T}\right) \tag{1}$$

2.5. Chemorheological models

The Arrhenius model is the predominant empirical model for the curing of thermosetting polymers. Assuming the Cox–Merz rule [31], the non–isothermal and isothermal Arrhenius models are described by Eqs. (2) and (3), respectively.

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

$$\mathrm{Ln}(\eta^*(t)) = \mathrm{Ln}(\eta^*_\infty) + \frac{\Delta E_\eta}{R \cdot T} + k_\infty \cdot \exp\left(\frac{-\Delta E_k}{R \cdot T}\right) \cdot t \tag{3}$$

An important drawback of the Arrhenius model is that it is handicapped for non-exponential changes in a resin's complex viscosity (the diffusion-controlled stage of the curing kinetics).

The Kiuna model has been proposed to describe the complex viscosity behavior of a material when diffusion increases its importance in the overall curing process, reducing the crosslinking rate. The Kiuna model, which assumes a different polynomial order for the change in a resin's complex viscosity with the cure time, has been used in modeling isothermal data. This model is also equivalent to the thermal shifting model of Fontana [32], and it can be applied to non-isothermal runs. The Kiuna model is based on the following expressions [26]:

$$\frac{d\eta^*}{dt} = \eta \cdot \left(\frac{k(T)}{g'(\alpha)} + \frac{1}{\eta^*_0} \cdot \frac{d\eta^*_0}{dT} \cdot \frac{dT}{dt}\right) \tag{4}$$

$$\alpha' = \mathrm{Ln}\left(\frac{\eta^*}{\eta^*_0}\right) \tag{5}$$

$$f(\alpha') = \tau \tag{6}$$

$$\tau = k(T) \cdot t \tag{7}$$

The kinetic parameters of resin curing are calculated by applying two single linear regressions when the complex viscosity of polymer is fitted to the Arrhenius model. Isothermal analysis of the resin's complex viscosity (η^*) values are plotted versus time. The first linear regression is applied in order to obtain the kinetic and viscous constants for the resin curing process, $k(T)$ and $\eta^*_0(T)$, respectively. The kinetic parameters of this process are determined by adjusting the logarithm of the kinetic constant isothermal values versus the inverse of the resin curing temperature.

In the Kiuna model, to calculate the kinetic constants of resin curing, a minimization algorithm of residual sum of squares (RSS) from Matlab® 2007 software was used.

The degree of the resin's mechanical cure (α) was calculated from the changes in its elastic modulus by using the following equation:

$$\alpha(t) = \frac{\log(G'(t)) - \log(G'(t_{(\alpha=0)}))}{\log(G'(t_{(\alpha=1)})) - \log(G'(t_{\alpha=0}))} \tag{8}$$

The elastic moduli of the fully cured and uncured resol resin were estimated for each one of temperatures. It was assumed that the initial degree of curing corresponds to the material's gel point ($\alpha_{\text{gel}} = 0.65$). The resin's curing degree at gelation was obtained by TMA and DSC combined techniques [33]. The modulus was calculated by applying a first order kinetic equation to the curing data of the resol resin obtained by DSC in a previous work [20].

3. Results and discussion

3.1. Diffusion stage onset on curing temperature

The complex viscosity profiles of the resol resin during its curing process at different temperatures are shown in Fig. 1. The lowest operating temperature was fixed at 80 °C. Below this temperature, the resin did not show a complex viscosity increase due to the curing reaction. The highest operating temperature was set at 100 °C because the water content of the resin causes dispersion in the complex viscosity measurements even after being precured beyond its gel point [34]. The water released during the polycondensation of the resin caused the bubbling off of the trapped gas, especially at high operating temperatures. The bubbles must be allowed to leave the material, which occurs when the viscous flow are sufficiently large to overcome the surface tension forces [35]. The dispersed data found when operating at temperatures over 100 °C were due to the gas diffuse out of the resin and the low free surface that the specimen has when parallel plates are used.

As seen in Fig. 1, the complex viscosity of the resin then started to rise after the curing temperature was reached due to the beginning of the crosslinking process. In addition, the curve of the resin complex viscosity does not present an inflection, which often is related to the change of the kinetics during the polymerization, particularly after the gel point [36]. This fact suggests that the curing degree of the precured resol resin was $\geq \alpha_{gel}$ [37]. The elastic moduli obtained were similar to the viscous moduli (Fig. 2), close to the crossover point at 25 °C (common rheological criteria to determine gelation), which confirms that the cure degree of resol resin was equal to that determined by TMA and DSC at the gelation point ($\alpha_{gel} = 0.65$) in a previous work [33].

The evolution of the logarithm of the resol resin's complex viscosity versus time at 95 °C (Fig. 3) showed a nonlinear change for the precured material. This deviation during the curing process is due to a diffusion stage that begins to control the overall process kinetics as the cure degree approaches the glass transition at the operating temperature [38,39]. The diffusion region onset time of the curing process for the resol resin has been defined as a 5% deviation from the linear behavior. Diffusion control of the resin curing kinetics took place at $T \geq 90$ °C.

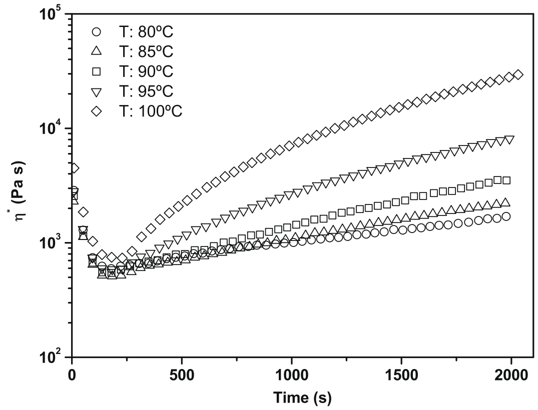

Fig. 1. Resin isothermal curing runs: η^* vs. time.

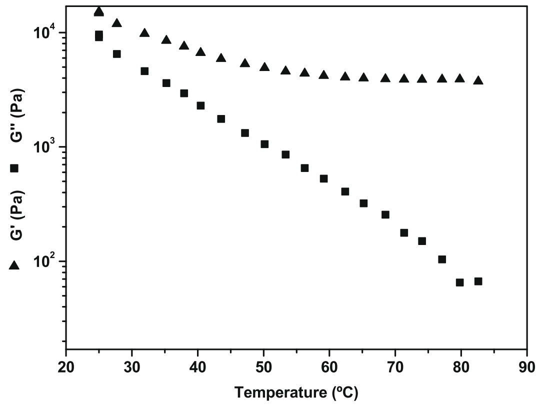

Fig. 2. Viscous and elastic moduli of the precuring resin during the heating ramp.

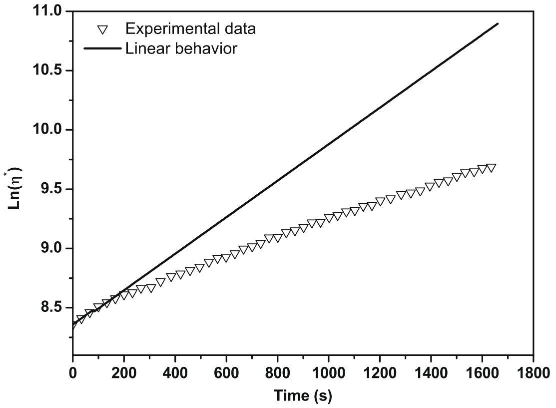

Fig. 3. Ln(η^*) deviation from linear behavior at 95 °C.

The curing degree of resol resin at the onset of the diffusion stage was calculated from the onset time determined at each curing temperature by applying the kinetic model for the resol resin curing reaction obtained by DSC in a previous work [20]. The curing degree profiles calculated for the resin at each operating temperatures by this model were assumed to be similar to the values obtained from the elastic modulus (G').

The parameter T_2 included in Eq. (1) was obtained from a curve fitting the resin onset degree of cure versus $1/T$ ($T_2 = 22.9$ °C). The TTT diagram of resol resin obtained in a previous work [30] ratifies the calculated T_2 value due to the glass-transition temperature of the uncured material ($T_{g0} = -5.5$ °C) and the low resin vitrification degree of cure at T_2. Thus, the beginning of the diffusion control region is due to the reduction of the resin chains' mobility as its curing degree approaches α_{max}. In the glassy state, the free volume of the resin decreases and only allows local motion of the chain segments [25].

3.2. Chemorheological modeling

The increase in the complex viscosity found during the isothermal curing step is the result of a decrease in the

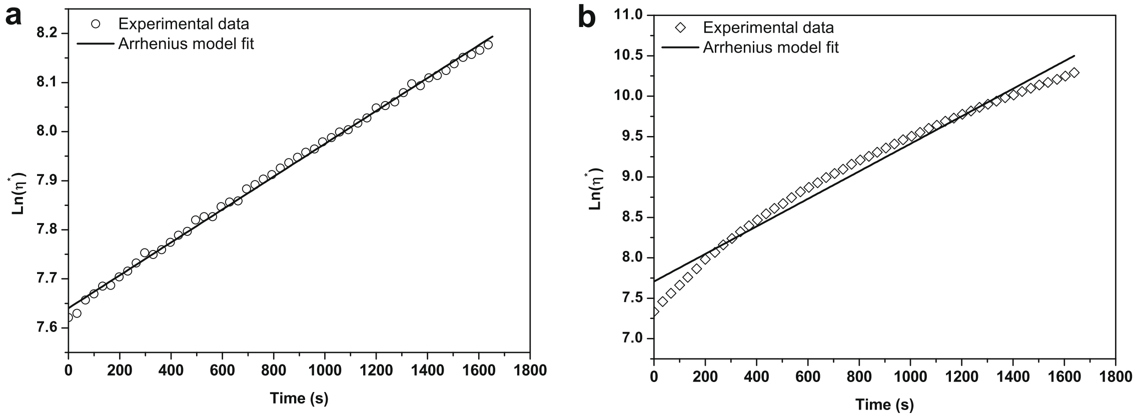

Fig. 4. Ln(η^*) vs. curing time for the Arrhenius model at: (a) 80 °C Experimental (open circles) and calculated (solid line). (b) 100 °C Experimental (squares) and calculated (solid line).

molecular mobility, which depends strongly on the polymerization mechanism (Fig. 1). The complex viscosity of the resol resin showed a similar behavior to the crosslinking step-growth polymerization system described by Van Assche et al. [15]. Thus, the complex viscosity of the resin rises continuously with extent of polymerization and no-different steps (initiator decomposition, propagation, and termination) take place. The diffusional limitations occurred that at $T \geq 90$ °C are non-specific and are related to the diffusion control of overall process kinetics. This decreases both the molecular mobility of resin and its polymerization rate [15]. In the crosslinking step-growth system, no marked decrease in the rate of resol resin cure should occur, as shown for the isothermal step (complex viscosity growing step) in Fig. 1.

The Arrhenius model was applied to complex viscosity values of the resol resin obtained from isothermal curing runs. The logarithm of the complex viscosities of the resol resin and the Arrhenius model predictions versus time are shown in Fig. 4 at the lowest (80 °C) and the highest (100 °C) operating temperatures tested.

The linear time dependence of the logarithm of resol resin complex viscosity is only valid at low temperatures (below 90 °C), when reaction kinetics of overall process is chemical controlled (Fig. 4(a)). The Arrhenius model cannot predict the complex viscosity changes of the resol resin at curing temperatures higher than 90 °C, when the diffusion control over the overall process kinetics causes a non-linear evolution of the material's viscosity. This is corroborated by the decrease of the statistical parameters for the fits (Table 1). As curing temperature increases, the experimental Ln(η^*) values (Fig. 4(b)) deviate from the linear behavior proposed by the Arrhenius model.

Table 1
Kinetic constants for all curing temperatures obtained from the Arrhenius rheological model.

T (°C)	Ln($k(T)$)	σ	R^2
80	−7.55	0.019	0.997
85	−7.14	0.022	0.998
90	−6.87	0.029	0.998
95	−6.62	0.084	0.992
100	−6.38	0.128	0.988

The kinetic parameters from the Arrhenius model application, the correlation coefficients, and the variances calculated for the curing process of the phenolic resin samples are exhibited in Table 2. The average E_k (activation energy) value of the resol resin is 72.1 kJ/mol. This is in accordance with literature values between 70.7 and 79.4 kJ/mol obtained when isoconversional methods are applied to the same material analyzed by DSC [20,33]. Nevertheless, the predicted viscosity profiles obtained at high temperatures ($T \geq 90$ °C) are in disagreement with the behavior of the experimental complex viscosity of the resin. Therefore, the Arrhenius model is only proposed as suitable to predict the resol resin curing behavior when diffusion does not become the controlling stage of the overall process kinetics (below 90 °C). At these low temperatures, the Arrhenius model describes first order kinetic behavior for the resol resin curing process.

The Kiuna model is proposed in order to obtain the kinetic parameters of resol resin curing when α_{onset} is overcome and diffusion stage controls the overall process kinetics [26]. The changes in the logarithm of the reduced complex viscosity of the resol resin (α') can be calculated by Eq. (5) and predicted by applying the Kiuna model for a second order polynomial. Both types of data are represented in Fig. 5 versus time for the highest operating temperature (100 °C). The second order polynomial parameter (a_1) of Eq. (6) is employed in a similar way to the "diffusion factor" proposed by Chern and Poehlein to improve the model accuracy [40]. This parameter, which is negative in order to predict the decreasing reaction rate of curing process of resol resin due to diffusion, enables the model to be applied for the diffusional control region.

Curing kinetic parameters of the resol resin for the Kiuna second order model are exhibited in Table 2. In relation to the Arrhenius model statistical values, the data fit to the Kiuna model reported superior correlation coefficients and a decrease of standard deviations by more than a decade.

The resol resin average E_k value (88.1 kJ/mol) attained by applying the Kiuna model is in agreement with the activation energy (89.0 kJ/mol) obtained by Ozawa

Table 2
Kinetic parameters of resin curing obtained from the Arrhenius and the Kiuna rheological models.

Sample	Arrhenius				Kiuna			
	E_k (kJ/mol)	Ln(k_∞)	σ	R^2	E_k (kJ/mol)	Ln(k_∞)	σ	R^2
1	62.9	13.92	0.052	0.995	85.4	21.65	0.029	0.999
2	77.4	18.31	0.164	0.969	87.2	21.72	0.014	1.000
3	76.1	18.03	0.149	0.973	87.2	21.72	0.014	1.000
Average	72.1	16.75	0.122	0.979	88.1	31.32	0.021	0.999

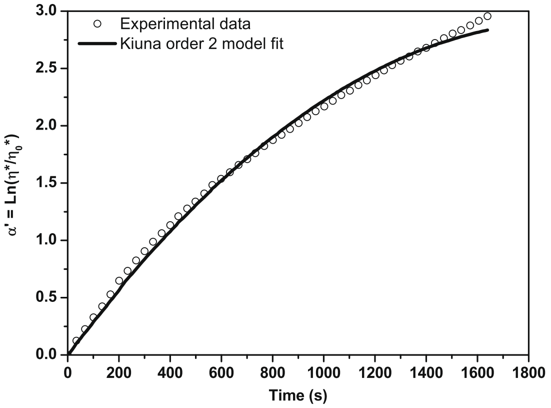

Fig. 5. The Kiuna order 2 model. Experimental (open circles) and predicted (solid line) values of α' vs. curing time at 100 °C.

isoconversional method for the same resol resin curing process under isothermal conditions [41]. This result is also in agreement with the literature concerning similar phenolic resins with degrees of cure higher than 0.6. For these resins, activation energies were between 80 and 90 kJ/mol when a free kinetics model was applied [42]. The activation energy found for the curing of the tested resol resin is also in the same E_k range obtained in the curing of phenolic novolac resins (62–116 kJ/mol) [42,43] and polyurethanes (43–85 kJ/mol) [44]. However, Perry determined a higher activation energy (124.0 kJ/mol) for the chemorheological curing of a resol resin powder by freeze-drying [45]. Note that a freeze-dried sample presents a lower water content in addition to a reduced mobility. The reduction of the water content in the resin produces a similar effect to a high crosslinking density reached as curing degree approaches to vitrification and the activation energy of the process for the same material becomes meaningfully higher.

The higher activation energy of the resol resin curing provided by the Kiuna model in relation to the value obtained from Arrhenius model is in accordance with the activation energies found in literature at high degrees of cure for an isoconversional kinetic method. In this case, the activation energy obtained by Cai et al. [46] for the curing of an epoxy resin increased from 30 to 50 kJ/mol for a conversion degree range between 0.6 and 1. In the same way, Sun et al. [25] developed an improved model to predict the kinetics of complex curing processes when diffusion becomes the controlling stage of overall process kinetics. For the curing of a lignin-based-epoxy/anhydride, the range of the activation energy found by Sun et al. spanned from 60.2 to 87.8 kJ/mol for a curing degree between 0.14 and 1. The E_k rising value determined by applying the isoconversional methods and Sun or Kiuna models is related to the increase of entanglements and molecular weight of the resin, thus reducing the polymer chains' mobility and producing a progressive decay of the reaction rate as the curing degree approaches $\alpha_{\max}$ [25,46]. The reduction of the chains' mobility in the material is due to the segments' difficulty in initiating translational motion, which is reflected by a large energy barrier to the segmental motion. When the resin curing degree reaches $\alpha_{\max}$, vitrification occurs for certain a crosslinking density at each operating temperature. At this point, the activation energy increases its value dramatically and the curing reaction of the resin stops entirely.

The profile of the curing degree of resol resin was determined from an experimental rheological variable (G') by applying Eq. (8). The curing degree of resol resin calculated from the elastic modulus G' is in accordance with the α values previously obtained by DSC measurements at 100 °C for the same material, as shown in Fig. 6 [20]. The relative deviation between the rheological and the DSC values for α is lower than 1% for all isothermal tests carried out, confirming the assumption that α calculated by DSC for each temperature is similar to α determined from G'.

As shown in Fig. 6, the increase in the curing degree of resol resin from 0.65 to 0.76 at the highest operating temperature (100 °C) is quite narrow. At this temperature, the low water content of resol resin and the degree of cure beyond its gelation point, $\alpha \geq 0.65$, do not allow for obtaining

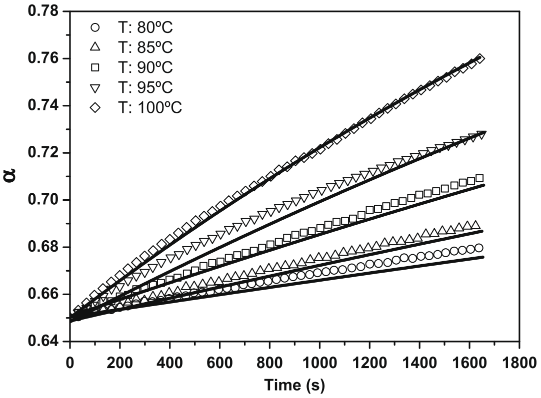

Fig. 6. Curing degree of resol resin calculated (open symbols) from elastic modulus (G') and obtained from DSC measurements (solid lines) [20] vs. curing time from 80 to 100 °C.

complete profiles for the degree of resin cure as tested by DSC and rheology.

The mechanical profile for the degree of conversion was similar to the chemical profiles obtained for resol resin cure [20]. This is because the sample support is coated with a silicon fluid that ensures a constant temperature profile, and the resin is in an environment where it will react in a similar way to resin measured via DSC. Ramis et al. also reported similar profiles for mechanical and chemical degrees of curing for a thermosetting powder coating made up of carboxyl-terminated polyester and triglycidylisocyanurate [47].

4. Conclusion

A non-linear change in the complex viscosity of the precured resol resin was observed during isothermal rheological tests at temperatures $T \geq 90\,^{\circ}\mathrm{C}$ when the Arrhenius model is applied. This behavior is due to diffusional control of the overall process kinetics, so the Arrhenius model was only suitable to predict the viscosity changes of resol resin when the curing kinetics was controlled by the chemical reaction ($T \leq 90\,^{\circ}\mathrm{C}$).

The Kiuna polynomial model is suggested to describe both chemical and diffusional stages of the curing process kinetics for a resol resin. The average activation energy obtained for resol resin curing was 88.1 kJ/mol, a value in good agreement with the literature. The higher activation energy obtained in this case compared to that obtained by applying the Arrhenius model is explained by the energetic constrains caused during the diffusional stage. The Kiuna model presents several important advantages. The curing degree of the resol resin is not required to apply the model, no limiting conversion had to be defined, and the chemorheological behavior of the resin is predicted by a single equation.

In short, the rheological behavior of the resol resin during the curing process has been described by application an appropriate chemorheological model, the Kiuna model. This model also permitted calculation of the kinetic parameters for the curing process of the resol resin. Finally, this work has shown that the degrees of mechanical and chemical curing of the resin are similar.

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