Thermochimica Acta 498 (2010) 39–44

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Kinetic study of a phenolic-novolac resin curing process by rheological and DSC analysis

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

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

ARTICLE INFO

Article history:
Received 13 August 2009
Received in revised form
16 September 2009
Accepted 22 September 2009
Available online 30 September 2009

Keywords:
Phenolic resin
Novolac
Curing
Chemorheology
Kinetics

ABSTRACT

Rheological isothermal curing runs of a novolac resin were performed in order to study its chemorheological behavior. In addition, DSC tests were carried out for the partially cured novolac resin to determine the curing degree reached at the end of each isothermal run. The Arrhenius and Kiuna empirical models were applied to establish the curing kinetic parameters of a novolac resin. The material curing process had an activation energy of 195.0 kJ/mol using the Arrhenius rheokinetic model. The activation energy obtained for the resin curing was 103.5 kJ/mol when the Kiuna model was applied. The profile of the resin's curing degree for all isothermal tests was obtained from rheological parameters: complex modulus (G^*), elastic modulus (G') and torque (Γ). Torque was the most suitable rheological variable of the resin for evaluating changes in the degree of cure during the curing process of the novolac resin. The Kamal and Markovic kinetic models were proposed to model the resin's curing behavior. Kamal's model was suggested as the best approach to predict the change in the mechanical degree of conversion during the material curing process.

1. Introduction

The curing of thermosetting materials is a complex process due to the interaction between the chemical kinetics and changes in their physical properties [1]. The study of the curing process kinetics of phenolic resins is important for understanding the material, to improve its final application, to develop new applications and materials, and to attain lower costs. In addition, due to obvious applications in molding processes, research on the mechanical response of thermosets has focused on measuring and modeling the development of resin velocity during the cure process [2].

The novolac resins are thermoplastic polymers and, by adding a curing agent, become a thermosetting material. Hexamethylenetetramine (HMTA) is the most widely used curing agent (source of formaldehyde) for curing processes of novolac resins [3–5].

The most important physical changes during material curing reactions occur when the gelation and vitrification stages take place. Gelation is the irreversible transformation from a viscous liquid to an elastic solid, which marks the first appearance of an infinite network. Vitrification is a reversible transition which is understood as a change from the liquid or rubbery state to the glassy state due to an increase in both the crosslinking density and the molecular weight of the polymer during the curing process of the material [6].

In this work mechanical properties are analyzed in order to study the curing kinetics of a novolac resin. Several chemorheological models for novolac resins have been presented in literature including empirical models, probability based models, gelation models, and models based on free volume analysis [7–12].

The changes in a resin's degree of cure (α) during its curing process are usually followed by thermal analysis techniques such as DSC. The profiles of a material's curing degree are commonly linked to a rheokinetic model when a rheological technique is used to study the kinetics of the resin curing process.

The aim of this work is to determine the kinetic parameters of the curing process of a novolac resin. Two rheokinetic models, Arrhenius and Kiuna, are proposed in order to achieve it. DSC analysis is used to obtain the total reaction heat and the partially cured residual heat of the novolac resin and is employed to obtain its degree of cure after rheological tests. The profiles of the material's curing degree for several operating temperatures are calculated from the evolution of rheological parameters such as complex modulus (G^*), elastic modulus (G'), and torque (Γ) [7–9]. Autocatalytic and Markovic models were applied to the evolution of the mechanical curing degree of the resin calculated in order to achieve suitable predicted values.

2. Materials

The commercial novolac resin and the curing agent (HMTA) were supplied by Hexion Speciality Chemicals Ibérica, S.A. The

---

* Corresponding author.
E-mail address: jucdomin@quim.ucm.es (J.C. Domínguez).

0040-6031/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2009.09.010

main properties of the novolac resin were as follows: formaldehyde/phenol molar ratio 0.7, free phenol content < 0.2 wt.%, free formaldehyde content < 0.3 wt.% (ISO 9397), softening point between 115 and 125 °C (DIN 51920), water content < 0.4 wt.% (DIN 51777.1 and DIN 53715), and a flow distance of 25–40 mm (ISO 8619). The mixture of the novolac resin and 9 wt.% curing agent was ground using a MM301 Reztch® mill. Sample disks with a 2 mm thickness and a 25 mm diameter (Ø) were obtained by molding the milled mixture.

3. Instrumentation

Rheological runs were performed using an ARES Rheometer (TA Instruments®) with a 25 mm Ø upper serrated plate and a 42 mm Ø lower parallel plate. The lower plate was filled for sample immersion in a silicon surrounding fluid (Dow Corning 200® FLUID 100 cSt) to avoid different curing reaction rates across resin disks. The autotension option was enabled to prevent contact loss between sample and plates. Isothermal curing runs (95, 100, 105, 110, 115, 120 °C) were carried out for 15 min for a fixed frequency of 1 Hz. The initial temperature was 25 °C, and a 20 °C/min temperature ramp was programmed to reach 90 °C, so the glass transition temperature of the material ($T_{g_0} = 68.5$ [10]) was overcome. Samples were stabilized during the 2 min before the operating temperature was reached through a 10 °C/min heating ramp.

The calorimetric measurements were performed on a DSC (Mettler Toledo® 821^e) with pressure medium pans (ME-26929) with a volume of 120 μL. Cured novolac samples, from isothermal experiments performed in the rheometer, were dried and milled prior to the DSC analysis. DSC dynamic runs were carried out using a 10 °C/min ramp from 30 to 250 °C under a N_2 atmosphere.

4. Rheokinetic models

Arrhenius and Kiuna rheokinetic models were proposed to predict the complex viscosity behavior of the novolac resin. The Arrhenius model was applied as it is the most common empirical model, and Kiuna was proposed to overcome the drawbacks of the Arrhenius model.

4.1. Arrhenius model

The generic form of the Arrhenius model, assuming the Cox–Merz rule [11], is described by Eq. (1).

$$\ln(\eta^*(t,T)) = \eta_0^*(T) + k_\infty \int \exp\left(\frac{-\Delta E_\mathrm{k}}{RT}\right) \mathrm{d}t \tag{1}$$

where η^* is the complex viscosity at absolute temperature T, $\eta_0^*(T)$ is the viscous constant, R is the universal gas constant, k_∞ is the kinetic constant analogue of η_∞^*, and $-\Delta E_\mathrm{k}$ is the kinetic activation energy. The Arrhenius model is based on the following equation for isothermal analysis:

$$\ln(\eta^*(t)_T) = \ln(\eta_\infty^*) + \frac{\Delta E_\eta}{RT} + tk_\infty \exp\left(\frac{-\Delta E_\mathrm{k}}{RT}\right) \tag{2}$$

where η_∞^* is the reference viscosity at "infinite temperature" and ΔE_η is the Arrhenius activation energy for the complex viscosity.

The kinetic parameters of the novolac resin curing were calculated from the Arrhenius model by applying two single linear regressions. Isothermal analysis viscosity (η^*) values were plotted versus time. The first linear regression was applied in order to obtain kinetic and viscous constants, $k(T)$ and $\eta_0(T)$. The kinetic parameters of the resin curing were calculated by fitting kinetic constants versus the inverse value of all curing temperatures. Viscous parameters can be calculated from the viscous constant following the same procedure mentioned for $k(T)$. In addition, a minimization algorithm for the residual sum of squares (RSS) from the Matlab® 2007 software was used to calculate the parameters of the curing process simultaneously.

4.2. Kiuna model

The Kiuna model was proposed due to its improvements over the Arrhenius model. The evolution of the complex viscosity during the resin curing process is predicted by the model without requiring its degree of cure [12]. Viscosity data are used directly to simulate the variations in viscosity behavior and thus the determination of the cure kinetics of the material is not required.

The original method was developed by Fontana to be applied to isothermal curing, but proved less accurate when dealing with non-isothermal curing conditions [13]. For the latter, Fontana proposed the normalization of viscosity at temperature (T_i) to viscosity at reference temperature (T_r). Kiuna developed upon the Fontana model and suggested the possibility of a non-Arrhenius temperature dependence. Once the kinetic constant $k(T)$ was calculated, Arrhenius temperature dependence is assumed to obtain the kinetic parameters of the material curing process. The Kiuna model, which assumes a different polynomial order for the change in viscosity during the cure process, was also used in modeling isothermal data as follows [12]:

$$\frac{\mathrm{d}\eta^*}{\mathrm{d}t} = \eta\left[\frac{k(T)}{g'(\ln(\eta^*/\eta_0^*))} + \frac{1}{\eta_0^*}\cdot\frac{\mathrm{d}\eta_0^*}{\mathrm{d}T}\cdot\frac{\mathrm{d}T}{\mathrm{d}t}\right] \tag{3}$$

$$\alpha' = ln\left[\frac{\eta^*(T)}{\eta_0^*(T)}\right] \tag{4}$$

$$f(\alpha') = \tau \tag{5}$$

$$\tau = k(T)\cdot t \tag{6}$$

where τ represents the elapsed cure time, η_0 is the viscosity of the uncured resin at temperature T and $k(T)$ represents the rate of advance of the curing process at temperature T. For isothermal conditions, the model predicts the curing rate using the following expressions:

$$\alpha' = f(\tau) \tag{7}$$

$$f(\tau) = \tau + a_2\tau^2 + a_3\tau^3 \cdots + a_n\tau^n \tag{8}$$

A minimization algorithm for residual sum of squares (RSS) from the Matlab® 2007 software was used to calculate the parameters of the curing process simultaneously.

4.3. Kinetic analysis

The novolac resin was analyzed by DSC to obtain its curing heat release $(\Delta H_\mathrm{p})_\mathrm{t}$. The heat flow of the material crosslinking process was calculated as the area under the exothermic peak and used to determine the degree of conversion reached after being cured in the rheometer. Previously, the silicone surrounding fluid was analyzed by DSC to avoid possible interference and noises. A baseline was obtained to eliminate appreciable heat flow due to physical or chemical transitions. The material's degree of conversion can be obtained by the following expression:

$$\alpha = \frac{(\Delta H_\mathrm{p})_\mathrm{t}}{\Delta H_0} \tag{9}$$

where $(\Delta H_\mathrm{p})_\mathrm{t}$ is the heat released up to a time t, and ΔH_0 is the total reaction heat associated with the cure process.

The evolution of the material's curing degree was calculated according to different authors using some of the common rheological variables studied during the resin crosslinking process. A complex modulus (G^*) for isothermal chemorheological analysis (Eq. (10)) was assumed to describe the curing degree behavior [8]. Eqs. (11) and (12) were also proposed to obtain the curing degree of the novolac resin from the elastic modulus (G^*) [7,14]. In addition, torque (Γ) normalized values (Eq. (13)) for each temperature described the resin's degree of cure [9].

$$\alpha(t) = \frac{G^*(t) - G^*(t_{\alpha=0})}{G^*(t_{\alpha=1}) - G^*(t_{\alpha=0})} \tag{10}$$

$$\alpha(t) = \frac{\log(G'(t)) - \log(G'(t_{\alpha=0}))}{\log(G'(t_{\alpha=1})) - \log(G'(t_{\alpha=0}))} \tag{11}$$

$$\alpha(t) = \frac{1}{\int_0^{t_{\alpha=1}} (\mathrm{d}G'(t)/\mathrm{d}t)\mathrm{d}t} \int_0^{t_{\alpha=1}} \frac{\mathrm{d}G'(t)}{\mathrm{d}t}\mathrm{d}t \tag{12}$$

$$\alpha(t) = \frac{\Gamma(t) - \Gamma(t_{\alpha=0})}{\Gamma(t_{\alpha=1}) - \Gamma(t_{\alpha=0})} \tag{13}$$

where α represents the curing degree of the resin, $G^*(t)$ and $G'(t)$ are the complex and elastic modulus at time t, $G^*(t_{\alpha=0})$ and $G'(t_{\alpha=0})$ are the complex and elastic modulus for the uncured resin, and $G^*(t_{\alpha=1})$ and $G'(t_{\alpha=1})$ are the complex and elastic modulus for the fully cured resin, respectively. $\Gamma(t)$ refers to the measured torque of the novolac resin during the isothermal runs keeping the applied strain constant. The same naming terminology as for the elastic modulus was followed for this parameter in this study.

Complex and elastic moduli and torque values for the fully cured resin were estimated for each temperature by obtaining the final curing degree reached by the DSC. The profile of the novolac's curing degree was studied using general phenomenological models due to the extremely complex (in the case of phenolic resins analysis) mechanistic models; the high degree of complexity of the curing reaction involves the formation of a great number of intermediate compounds [15,16]. Phenomenological models based on the empirical curing degree values obtained previously were found to be more appropriate in this case [17,18]. Kamal's autocatalytic model (Eq. (14)) and Markovic's model (Eq. (15)) are commonly used to describe thermosetting curing behavior [19]. These models were proposed to analyze the evolution of α obtained for the resin:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k\alpha^m(1-\alpha)^n \tag{14}$$

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(1-c\alpha)(1-\alpha)^2 \tag{15}$$

where α is the rheological degree of conversion, t is time, k is the kinetic constant, c is a temperature-dependent constant, n is the reaction order and m is the autocatalytic reaction order for Kamal's model ($m+n=2$).

5. Results and discussion

5.1. Rheokinetic modeling

Experimental and predicted values from the Arrhenius model at 120 °C are plotted versus time in Fig. 1.

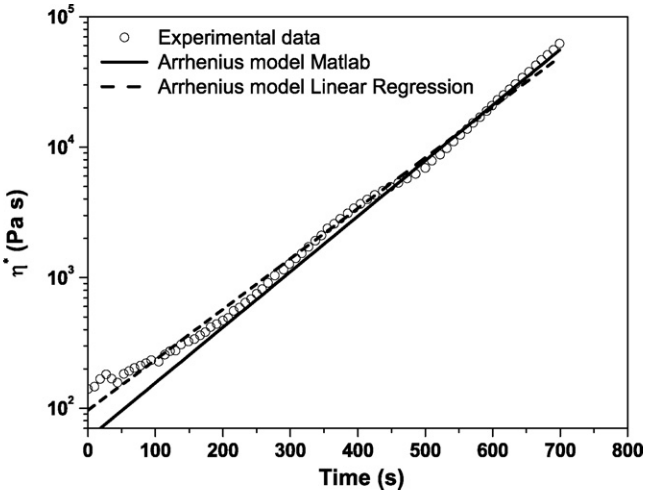

Fig. 1. Complex viscosity versus curing time for the Arrhenius model at 120 °C.

Table 2
Activation energies and statistical parameters for the Kiuna rheokinetic model.

	Kiuna	ΔE_k (kJ/mol)	RSS	σ^2
Novolac resin	Order 1	55.8	281.10	0.663
	Order 2	103.5	8.61	0.019

The resin's complex viscosity showed a rapid increase with time due to the high rate of the curing process at 120 °C. A slight deviation from the linear behavior predicted by the Arrhenius model was found, which is attributed to gelation, but was overcome and α was close to the α_v (vitrification degree of cure) value at this temperature. The statistical coefficients, RSS and variance for the Arrhenius model fit were calculated as exhibited in Table 1.

The residual minimization method yielded more precise results than multiple linear regressions. The kinetic parameters of the novolac resin calculated by the Arrhenius model were 195.1 kJ/mol for the flow activation energy (ΔE_η) and 131.5 kJ/mol for the kinetic activation energy (ΔE_k). The last parameter is within the range of values (121–167 kJ/mol) obtained by nth order models [20–22]. In addition, isoconversion methods, commonly used in the determination of curing activation energies for thermosetting polymers by DSC, closely agreed (112–120 kJ/mol) with the obtained activation energy [23].

The Kiuna model was proposed in order to obtain more accurate kinetic parameters [12]. The evolution of the novolac resin's complex viscosity and predicted values from the Kiuna model at the isothermal curing temperature of 120 °C are shown in Fig. 2.

The activation energies of the Kiuna rheokinetic model were determined for both applied polynomial orders of the model (Table 2). The RSS and variance values decreased considerably when a second order polynomial was applied to the resin's normalized complex viscosity behavior.

Table 1
Statistical parameters of the novolac resin curing process for the Arrhenius model.

		Temperature (°C)						Total
		95	100	105	110	115	120	
RSS	A.M.F[a]	3.81	12.56	23.75	4.08	7.97	7.09	3.23
	A.M.L.R[b]	4.51	13.16	12.96	13.82	8.68	65.80	118.92
σ^2	A.M.F	0.051	0.170	0.321	0.055	0.108	0.096	0.133
	A.M.L.R	0.061	0.178	0.175	0.187	0.117	0.889	0.268

[a] Arrhenius Matlab fit.

[b] Arrhenius multiple linear regression.

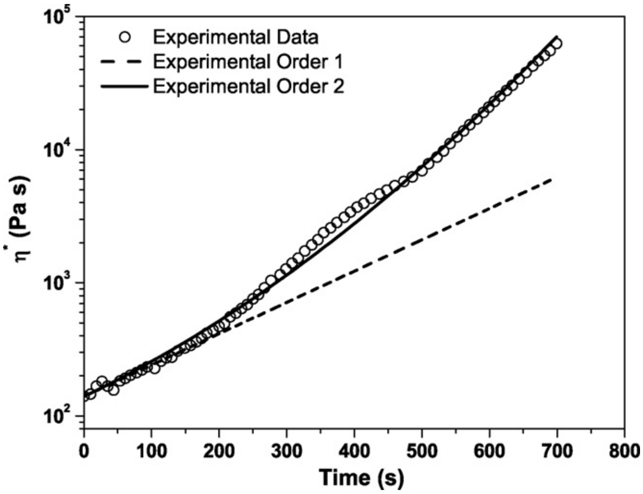

Fig. 2. Complex viscosity versus curing time for the Kiuna model at 120 °C.

The material's activation energy of the curing process for a first order model was substantially lower than the value determined by the Arrhenius model, and it was in disagreement with the values predicted for novolac resins by DSC (114–120 kJ/mol) [23]. This model polynomial order was discarded according to statistics parameters and literature-reviewed data (70–167 kJ/mol) [22–24]. Nevertheless, epoxy-novolac and other mixed novolac resins showed closed activation energies when the autocatalytic kinetic model was applied (57.5–67.2 kJ/mol) [23–25], and for isoconversion methods (79.7–81.3 kJ/mol) [26]. The addition of lignosulfonates to the novolac resin formulation also reduced the activation energy of the resin process as shown by Pérez [10].

The Kiuna model, when applied as a second order polynomial, increased kinetic parameters by adding a polynomial coefficient a_1 to the model. The a_1 calculated value was 0.044; the kinetic model was completely described. The kinetic activation energy for the material curing was slightly lower than the Arrhenius activation energy, but in accordance with the literature [22–24]; the statistic parameters were excellent. The lower value obtained for the activation energy with respect to the first order Kiuna model was related to the high degrees of transformations reached, which is more characteristic of the solid-state diffusion [27]. Thus, the Kiuna model, when applied to the novolac resin's complex viscosity advance during the curing process, reveals a shift from the kinetic to diffusion regime that took place for the highest operating temperatures, as the low value of a_1 proved.

5.2. DSC analysis

The total curing heat flow (ΔH_T) was determined by DSC measurements of the uncured resin. The partially cured novolac resins from the isothermal rheological tests were analyzed by a dynamic DSC test in order to obtain its residual heat of curing. The novolac's degrees of cure reached at all rheological operating temperatures were obtained from the rate between partially and fully cured resins, as shown in Table 3.

The resin's curing degree behavior calculated at 115 °C according to the methods proposed is exhibited in Fig. 3. Significantly different behaviors for α were found when Eq. (11) was applied and calculated values were compared to the curing degree advance obtained by Eqs. (10), (12) and (13) from several rheological variables. In addition, curing degree values obtained from the elastic modulus by Eqs. (11) and (12) showed a significant difference depending on the expression adopted for the calculations.

Table 3
Partial reaction heat and curing degree of the novolac resin obtained by DSC.

Temperature (°C)	$(\Delta H_p)_t$ (W °C/g)	α (%)
95	2.16	13.29
100	2.37	14.58
105	3.39	20.86
110	4.22	25.97
115	7.15	44.00
120	12.98	79.88
ΔH_T (W °C/g)	16.25	100

The torque method defined by Eq. (13) was chosen as more accurate due to the non-dependence on the sample's size. During the novolac curing process chemical shrinkage takes place. Thus, complex and elastic modulus measurement errors increase as the sample's geometry changes. These errors are related to the torque obtained by the fixed strain applied to the material, and also to the geometry of the sample. The autotension option allowed for the evaluation of changes in the resin's length, but changes in the diameter of the material were not measured. Despite the chemical shrinkage of the material, which in some resins such as hydroxyethyl methacrylate-polyurethane (HEMA-PU) and unsaturated polyester is close to 15% of the volume [28,29], does not involve a great error, torque profiles become a more accurate way to describe the evolution of the material's curing degree as long as the applied strain for isothermal analysis is kept constant. The elastic modulus integral and logarithm methods presented an increasing dispersion in the calculated curing degree values of the resin as the operating temperature decreased. The complex modulus approach Eq. (10) disagreed with the curing degrees calculated from the measured torque due to the high values presenting an oscillating behavior of α at temperatures below 110 °C. The novolac's curing degree obtained by the torque method with Eq. (13) versus time at the highest temperatures (110–120 °C) is shown in Fig. 4.

5.3. Isothermal kinetic models

The autocatalytic and Markovic models applied to the evolution of the resin's degrees of cure calculated from Eqs. (10) and (13), respectively, at 120 °C curing isothermal runs are shown in Fig. 5. The polymer's degree of cure was modeled beyond the gelation point ($\alpha_{gel} = 0.52$) obtained in previous works for this novolac resin [23]. The postgelation regime during the material curing pro-

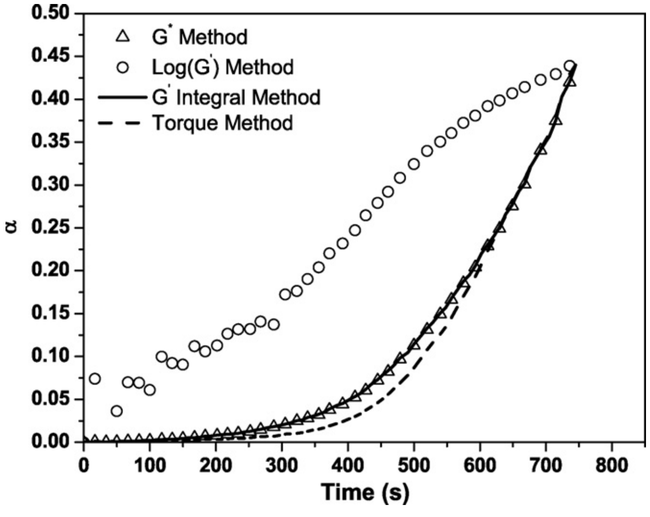

Fig. 3. Evolution of the novolac resin's degree of curing at 115 °C.

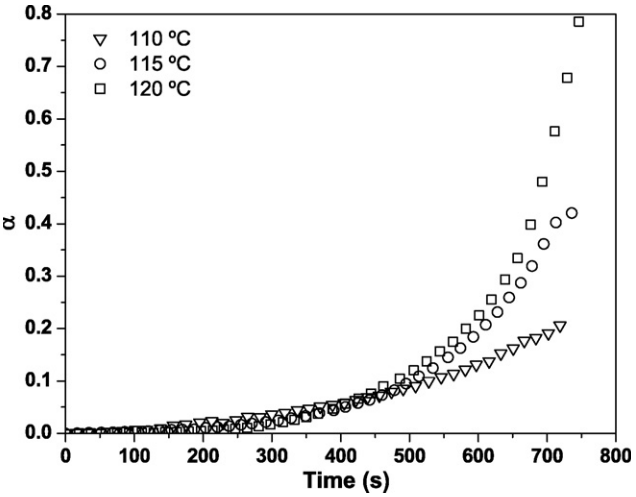

Fig. 4. Curing degree behavior of the material obtained from torque values.

cess is highly related to a possible diffusion-controlled stage over the kinetics of the resin curing process [30,31]. Therefore, diffusion control kinetic models applied in this case [32–36].

The kinetic constant for each model applied to α values obtained for the highest curing temperature (120 °C) and statistical parameters calculated for the novolac resin curing process are exhibited in Table 4.

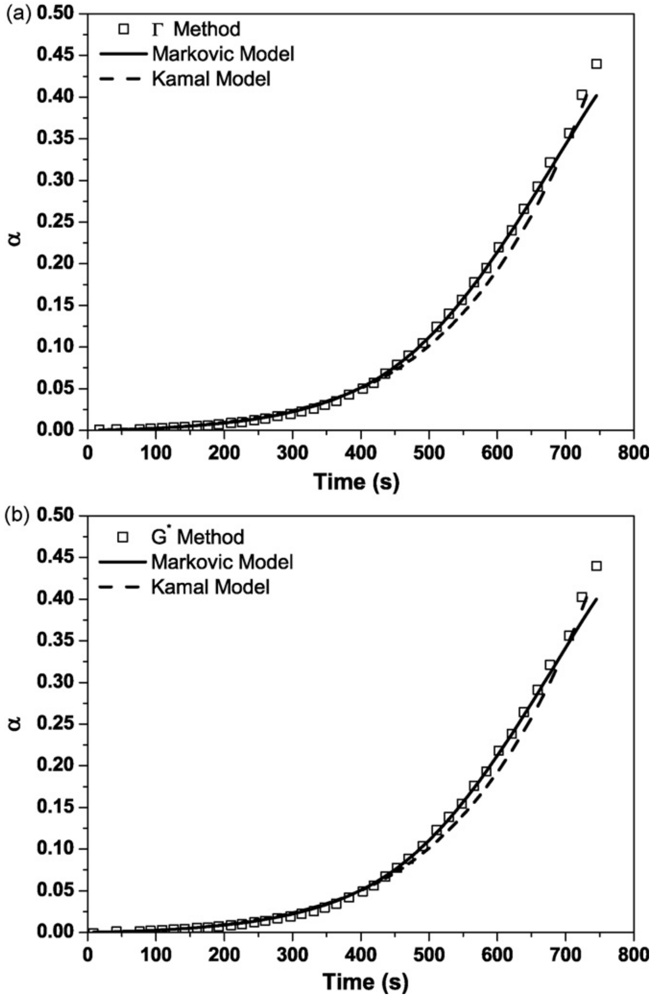

Fig. 5. Kinetic models applied to curing degree values calculated 150 °C from: (a) Complex modulus (G^*) and (b) Torque (Γ).

Table 4

Parameters of the resin curing process for Kamal and Markovic models obtained at 120 °C.

	G^*			Γ		
	$\ln(k)$ (s^{-1})	m	n	$\ln(k)$ (s^{-1})	m	n
Kamal	−4.811	0.898	1.102	−5.393	0.727	1.237
		RSS	15.558			62.336
		σ^2	0.126			0.854
	$\ln(k)$ (s^{-1})		c	$\ln(k)$ (s^{-1})		c
Markovic	−12.674		3838	−12.228		2394
		RSS	16.439			19.500
		σ^2	0.228			0.267

The c parameter of the Markovic's model was higher than values found in literature when this model was applied to a novolac resin ($3.95 \leq c \leq 13.74$; $n = 2$) [37]. This disagreement suggested that the Kamal autocatalytic model was as a better choice for this novolac resin. A better approach to calculated α values was reached when values obtained from the complex modulus method were fit by Kamal's model. This could be explained by the lower degrees of cure obtained. Nevertheless, Kamal's model was the best approach when applied to a curing degree range below 0.35, calculated from torque as is shown in Fig. 5. The kinetic constants, m and n are in accordance with the literature ($m + n = 2$) [19,38]. This suggests that the autocatalytic model is a good approach to apply to the novolac curing reaction. The self-acceleration character of this process could be a consequence of the crosslinking reaction and the morphological changes.

6. Conclusions

The Arrhenius model was more accurate when the least squares algorithm was applied in order to fit the experimental data for all isothermal runs. The flow and curing activation energies agreed with literature values for novolac resins.

The Kiuna model improved fits when the second order polynomial form was applied. E_k was close to previously obtained values for the Arrhenius model (131.5 kJ/mol); therefore, the curing activation energy was in the range of the literature values.

The curing degree advance was calculated by four different expressions and three rheological parameters were involved after the DSC final degree of cure for each isothermal run was obtained. The torque method was more accurate, and the elastic modulus integral and logarithm methods presented increasing dispersion in curing degree values as the curing temperature decreased. The complex modulus approach agreed with curing degree values calculated from G' integral method but dispersion was not present for low temperatures; therefore, it is useable, although the calculations are more complex than those for the torque method.

The Kamal autocatalytic kinetic model showed good agreement when it was applied to curing degree values previously obtained from the torque and complex modulus. Lower degree values were obtained when the complex modulus expression was used to calculate them, involving a significant reduction in the statistical fit parameters. When the Kamal model was applied to low range α values acquired from torque measurements, excellent agreement with the model was found.

Acknowledgments

The authors are grateful to the “Ministerio de Ciencia e Innovación” for financial support (projects CTQ2004-02031/PPQ and CTQ2007-64071).

References

[1] M.V. Alonso, M. Oliet, J.M. Pérez, F. Rodríguez, J. Echeverría, Thermochim. Acta 419 (2004) 161–167.
[2] D.J. O'Brien, P.T. Mather, S.R. White, J. Compos. Mater. 35 (2001) 883–904.
[3] A. Gardziella, L. Pilato, A. Knop, Phenolic Resins, Springer, 2000.
[4] A. Knop, L.A. Pilato, Phenolic Resins, Springer, 1985.
[5] R.W. Martin, The Chemistry of Phenolic Resins, John Wiley & Sons, 1956.
[6] L.H. Sperling, Introduction to Physical Polymer Science, John Wiley & Sons, 1992.
[7] M. Auad, S. Nutt, P. Stefani, M. Aranguren, J. Appl. Polym. Sci. 102 (2006) 4430–4439.
[8] J. Martin, J. Laza, M. Morrás, M. Rodríguez, L. León, Polymer 41 (2000) 4203–4211.
[9] D. Nichetti, Eur. Polym. J. 40 (2004) 2401–2405.
[10] J.M. Pérez, Estudio Del Curado De Resinas Ligno-Novolacas, Propiedades Termo-Mecanicas De Los Productos Curados, Universidad Complutense de Madrid, Madrid, 2005.
[11] W. Cox, E. Merz, J. Polym. Sci. 28 (1958) 619–622.
[12] N. Kiuna, C. Lawrence, Q.P.V. Fontana, P. Lee, T. Selerland, P. Spelt, Compos. Pt. A: Appl. Sci. Manuf. 33 (2002) 1497–1503.
[13] Q.P.V. Fontana, Compos. Pt. A: Appl. Sci. Manuf. 28 (1998) 153–158.
[14] M. Hargis, B.P. Grady, L. Aktas, K.R. Bomireddy, S. Howsman, M.C. Altan, T. Rose, H. Rose, J. Compos. Mater. 40 (2006) 873–897.
[15] A. Cadenato, J. Salla, X. Ramis, J. Morancho, L. Marroyo, J. Martín, J. Therm. Anal. Calorim. 49 (1997) 1429–1433.
[16] B.D. Park, B. Riedl, E.W. Hsu, J. Shields, Polymer 40 (1999) 1689–1699.
[17] M.V. Alonso, M. Oliet, J. García, F. Rodríguez, J. Echeverría, Chem. Eng. J. 122 (2006) 159–166.
[18] M.K. Um, I.M. Daniel, B.S. Hwang, Compos. Sci. Technol. 62 (2002) 29–40.
[19] M.R. Kamal, S. Sourour, Polym. Eng. Sci. 13 (1973) 59–64.
[20] T.R. Hwang, S.M. Lee, Y.S. Song, J.W. Lee (Eds.), The Study of the Novolac Type Phenolic Resins: Cure Characteristics and Mechanical Properties, Society of Plastic Engineers, ANTEC, 2004.
[21] C. Peña, M.D. Martin, A. Tejado, J. Labidi, J.M. Echeverría, I. Mondragón, J. Appl. Polym. Sci. 101 (2006) 2034–2039.
[22] J. Wang, M.P.G. Laborie, M.P. Wolcott, Thermochim. Acta 439 (2005) 68–73.
[23] J.M. Pérez, M. Oliet, M.V. Alonso, F. Rodríguez, Thermochim. Acta 487 (2009) 39–42.
[24] D. Mourant, B. Riedl, D. Rodrigue, D.Q. Yang, C. Roy, J. Appl. Polym. Sci. 106 (2007) 1087–1094.
[25] A. Tejado, G. Kortaberría, J. Labidi, J.M. Echeverría, I. Mondragón, Thermochim. Acta 471 (2008) 80–85.
[26] S. Ren, Y. Lan, Y. Zhen, Y. Ling, M. Lu, Thermochim. Acta 440 (2006) 60–67.
[27] S. Vyazovkin, Thermochim. Acta 223 (1993) 201–206.
[28] X. Cao, L.J. Lee, Polymer 44 (2003) 1507–1516.
[29] S.P. Lin, J.H. Shen, J.L. Han, Y.J. Lee, K.H. Liao, J.T. Yeh, F.C. Chang, K.H. Hsieh, Compos. Sci. Technol. 68 (2008) 709–717.
[30] T.H. Hou, J.Y.Z. Huang, J.A. Hinkley, J. Appl. Polym. Sci. 41 (1990) 819–834.
[31] G. Van Assche, E. Verdonck, B. Van Mele, Polymer 42 (2001) 2959–2968.
[32] Y.T. Chen, C.W. Macosko, J. Appl. Polym. Sci. 62 (1996) 567–576.
[33] M. Ivankovic, L. Incarnato, J.M. Kenny, L. Nicolais, J. Appl. Polym. Sci. 90 (2003) 3012–3019.
[34] F. Perrin, T. Nguyen, J. Vernet, Eur. Polym. J. 43 (2007) 5107–5120.
[35] G. Sun, H. Sun, Y. Liu, B. Zhao, N. Zhu, K. Hu, Polymer 48 (2007) 330–337.
[36] L. Zhao, X. Hu, Polymer 48 (2007) 6125–6133.
[37] S. Markovic, B. Dunjic, A. Zlatanic, J. Djonlagic, J. Appl. Polym. Sci. 81 (2001) 1902–1913.
[38] M.R. Kamal, Polym. Eng. Sci. 14 (1974) 231–239.