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Gelation and isoconversional kinetic analysis of lignin–phenol–formaldehyde resol resins cure

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Abstract

The curing process of a commercial phenolic (PF) and a lignin–phenolic (LPF) resol resins was studied by thermal mechanical analysis (TMA) and differential scanning calorimetry (DSC) techniques. The main conclusion that we wish to point out is that the gelation can be associated with an isoconversional principle. Thus, the curing kinetics analysis was performed applying non-isothermal DSC data to the isoconversional methods: Ozawa, Kissinger–Akahira–Sunose, and Friedman. These isoconversional methods allowed the determination of the dependence of activation energy and pre-exponential factor on the degree of curing for both resins. Friedman's method presents different results in relation to other methods, but both resins exhibit a similar tendency for kinetic parameters.

Keywords: Kinetics; DSC; TMA; Gelation; Cure; Phenolic resins

1. Introduction

Phenol–formaldehyde (PF) resins, either in liquid or solid form, are widely used in the manufacture of wood panel products. Ways to reduce its relatively high cost and formaldehyde emissions are sought by the industry. The incorporation of modified lignin in the formulation of PF resins is being developed as a means of lowering the cost of these [1–3]. Lignin can be obtained by different pulping processes, but only lignosulfonates are available in great quantities. Among them, the ammonium lignosulfonate has been reported to be the most adequate to formulate PF resins due to its higher reactivity towards formaldehyde than other lignosulfonates [4–6]. Once the synthesis of lignin–phenolic resol resin is optimized, then the next most expensive step is the resin cure process. Therefore, a reduced cure time has a strong influence on both the reduction of unit costs and productivity of panel manufacture.

The curing of thermoset resins is complex due to the interaction between the chemical kinetics and changes in their physical properties. The most important changes due to the material curing are gelation and vitrification. Gelation occurs at a well-defined and often calculable stage in the course of the chemical reaction and is dependent on the functionality, reactivity, and stoichiometry of the reactants. This sudden and irreversible transformation from a viscous liquid to an elastic gel, which marks the first appearance of the infinite network (molecular gelation), is called the gel point. The macroscopic consequences of gelation are that the viscosity tends to infinity and elastic properties of the material are acquired and are not present in the pre-gel state. Another phenomenon which may occur at any stage during cure and is distinct from gelation is vitrification of the growing 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 [7,8].

For thermosetting systems in industrial application, it is important to relate the transition phenomena (e.g., gelation or vitrification) to the reaction time at different cure temperatures so that desired properties can be controlled. When these transitions proceed, the thermosetting decreases its workability. Thus, the study of the cure kinetics contributes both to a better knowledge of the process development and to improving the quality of the final product.

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The methods used to study the cure kinetics can be classified in mechanistic or phenomenological terms. Mechanistic models are made from the balance of chemical species involved in the chemical reaction. In most cases, it is difficult to derive a mechanistic model because the resin cure reaction is very complex. Thus, phenomenological or empirical models are preferred to study the cure kinetics of these polymers [9]. Among them, there are several different methodologies for the determination of the curing kinetics of thermosetting materials; these are described as follows.

Traditionally, kinetic parameters were calculated from isothermal data by DSC. The advantage of these measurements was a complete separation between the variables of temperature and time. However, under these circumstances, the equipment neither reached nor stabilized at the desired temperature. Thus, an alternative is the utilization of dynamic data by DSC. So, there are direct methods such as Borchardt–Daniels [10], which employs a single dynamic scan by differential scanning calorimetry (DSC) to determine the kinetic parameters. There are models-free such as the Ozawa and Kissinger's models [11,12], which relate the heating rates (β) employed to the peak exothermic temperatures (T_p) of the different thermograms to obtain the activation energy of overall cure process. Since the phenolic resins are systems so complex that their activation energies change with conversion degree during the curing process, the isoconversional methods present the most accurate results. These methods reveal changes in the curing kinetics throughout the process. More detailed information is provided elsewhere [13–17].

To date the isoconversional methods have been applied to the cure of epoxy, epoxy-amine, and unsaturated polyester resins by dynamic DSC [18,19]. However, these methods have not been used on phenolic resins. The aim of this paper is to show that the phenolic and lignin–phenolic resins attain the same degree of conversion when resins reach the point gel measured by TMA technique. In addition, the isoconversional behavior of these resins allows applying specific methods to determine the curing kinetics of both thermosetting polymers by dynamic DSC.

2. Isoconversional methods

The reaction rate equation utilized to study the resins curing kinetics can be expressed, in general, as:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = kf(\alpha) \tag{1}$$

Considering that the rate Eq. (1) is valid for dynamic curing and that $\mathrm{d}\alpha/\mathrm{d}t = \beta(\mathrm{d}\alpha/\mathrm{d}T)$, where β is the heating rate (K/min), k the rate constant expressed by Arrhenius equation, which is a function of temperature, and $f(\alpha)$ is the reaction model, Eq. (1) can be written as:

$$\beta\frac{\mathrm{d}\alpha}{\mathrm{d}T} = A\mathrm{e}^{(-E/RT)}f(\alpha) \tag{2}$$

where T is the temperature, A the pre-exponential factor, E the activation energy which is independent of conversion, R the gas constant, and α is the cure degree. In this way, the integral form of the rate equation can be expressed as:

$$g(\alpha) = \frac{A}{\beta}\int_0^{T_\alpha} \mathrm{e}^{(-E/RT)}\mathrm{d}T = \frac{A}{\beta}P(E, T_\alpha) \tag{3}$$

where $g(\alpha) = \int_0^\alpha \mathrm{d}\alpha/f(\alpha)$ is the integrated form of the reaction model. To compute Arrhenius parameters, dynamic conditions, there are several relationships, each of which is based on an approximate form of the temperature integral (Eq. (3)). Assuming that $P(E/RT)$ can be expressed in the 20–60E/RT range as follows [20]:

$$\log P\left(\frac{E}{RT}\right) = -2.315 - 0.4680c\frac{E}{RT} \tag{4}$$

where c is initially 1.052; however, this value has been recalculated in an iterative procedure after the activation energy is estimated.

In order to determine the kinetic parameters, Eqs. (3) and (4) can be combined and rearranged as:

$$\log\beta = A' - 0.4567\frac{E}{RT} \tag{5}$$

where $A' = \log(AE/g(\alpha)R) - 2.315$. The expression (5) is known as Ozawa's method [11,21], which can be applied to different degrees of conversion. Thus, for a given degree of conversion, according to Eq. (5), the activation energy and the constant A' can be calculated from the slope and the ordinate, respectively, of the linear relation between $\log\beta$ and $1/T$.

Another expression similar to that proposed by Ozawa is the Kissinger–Akahira–Sunose's model-free [22], which may be originally obtained through derivation of Eq. (2) as follows:

$$\frac{\mathrm{d}^2\alpha}{\mathrm{d}T^2} = \left[\frac{\mathrm{d}f(\alpha)}{\mathrm{d}\alpha}A\mathrm{e}^{-E/RT} + \frac{\beta E}{RT^2}\right] \tag{6}$$

the term of right (Eq. (6)) is equal to 0 at the peak temperature, rearranging the terms and applying logarithm to Eq. (6), the expression obtained is the following:

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{RA}{Eg(\alpha)}\right) - \frac{E}{R}\frac{1}{T} \tag{7}$$

In this case, neither method requires knowledge of the conversion-dependence function ($f(\alpha)$ or $g(\alpha)$) and only presupposes that for a given degree of conversion the reactive process has the same mechanism of reaction, regardless of the curing temperature.

Friedman's isoconversional method [23] relates the logarithm of reaction rate to the inverse temperature for a given cure degree. In this way, the expression (1) and Arrhenius equation are rearranged as follows:

$$\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_i = f(\alpha_i)A_\alpha\mathrm{e}^{-E_\alpha/RT\alpha,i} \tag{8}$$

where the subscript α is referred to the value at a particular conversion and 'i' is referred to data from a given heating rate run.

Thus, from the logarithmic form of the rate Eq. (8) each of heating rates can be written as:

$$\ln\left[\beta_i\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_{\alpha,i}\right] = \ln[f(\alpha_i)A_\alpha] - \frac{E_\alpha}{RT_{\alpha,i}} \tag{9}$$

When a dynamic method is applied, the typical basic parameters $\mathrm{d}\alpha/\mathrm{d}t$ and α are required and can be obtained from the thermogram. The reaction rate is obtained by dividing the peak height $\mathrm{d}H/\mathrm{d}t$ at time t by the total heat of curing reaction, ΔH_0. Due variations in ΔH_0 with heating rate and temperature; an average value of this parameter is taken from nine different heating ramps. The reaction rate equation can be expressed as follows:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \frac{\mathrm{d}H/\mathrm{d}t}{\Delta H_0} \tag{10}$$

The α value is determined in dynamic runs as the ratio between the heat released up to a time t $(\Delta H_\mathrm{p})_t$, and the total heat of the reaction, ΔH_0:

$$\alpha = \frac{(\Delta H_\mathrm{p})_t}{\Delta H_0} \tag{11}$$

In the case of isothermal curing processes, degree of conversion is determined as:

$$\alpha = 1 - \frac{(\Delta H)_{t,\mathrm{res}}}{\Delta H_0} \tag{12}$$

where $(\Delta H)_{t,\mathrm{res}}$ is the residual heat obtained after isothermal curing up to a time t.

3. Experimental

3.1. Materials

Phenolic commercial resin (PF) tested was supplied from Hexion Speciality Chemicals Ibérica (Spain). This product is obtained by the reaction between phenol and formaldehyde in alkaline medium. Lignin–phenolic resol resin (LPF) was synthesized in laboratory from methylolated softwood ammonium lignosulfonates. The operating conditions of methylolation and formulation of lignin–phenolic resol resin were reported in previous works [6,24].

3.2. TMA measurements

To measure a sample length as a function of temperature or time, a Mettler Toledo TMA 840$^\mathrm{e}$ analyzer was employed. TMA can be used to characterize the change of resin from liquid to solid (gelation). The liquid resin was placed between two silica disks (ME-29595). The temperatures tested were 110, 120, 130, 135, and 140 °C. A periodic force (cycle time = 12 s) of ±0.03 N was automatically applied to the sample. Due to this force, the probe is moved up and down while the resin is still liquid. When the material reached the gelation, then the TMA measuring sensor was unable to respond to the force applied. At this moment, the sudden decrease in the amplitude of the oscillations reveals that the sample has attained the gelation. Then, the sample is cooled (T = 4 °C) and a dynamic scan by DSC is performed at a heating rate of 10 °C/min to determine the residual heat and the gel conversion by Eq. (12).

3.3. DSC measurements

The calorimetric measurements were performed with a differential scanning calorimeter (Mettler Toledo DSC 821$^\mathrm{e}$) under an atmosphere of N_2 (flow rate = 50 ml/min). Pans utilized were pressure medium (ME-26929) and samples size was 12–14 mg. The pans, with a volume of 120 μl, can withstand vapour pressures up to 10 MPa. Since it was difficult to weigh the same amount of sample in all cases, different thermograms were normalized, by the calorimeter software, at 1 g. Later, the baseline “spline” was subtracted from the original thermogram. Isoconversional methods were conducted under a nitrogen atmosphere at heating rates of 2, 4, 6, 8, 10, 12, 14, 16, and 20 °C min^{-1} in a scanning temperature range from 30 to 250 °C. The data of runs were fitted to Ozawa, Kissinger–Akahira–Sunose, and Friedman’s isoconversional methods.

4. Results and discussion

4.1. Validation of isoconversional principle

The extent of curing reaction at gel point (α_gel) with respect to different cure temperatures of the phenolic and lignin–phenolic resol resins is shown in Fig. 1. These data have been measured using the TMA technique, as described before. The TMA runs were stopped when the material attained the approximate gelation state. Actually, the TMA measures the shrinkage of the resol resin during curing. Thus, the thermoset keeps shrinkage proportional to the curing process, when the resin gels and obtains mechanical stability. At this moment, the sample is cooled rapidly to measure both the residual heat and the degree of gel conversion by DSC. It is observed that although the time taken by the resin to reach the gel point varies with the temperature, the α_gel values is independent of the curing temperature

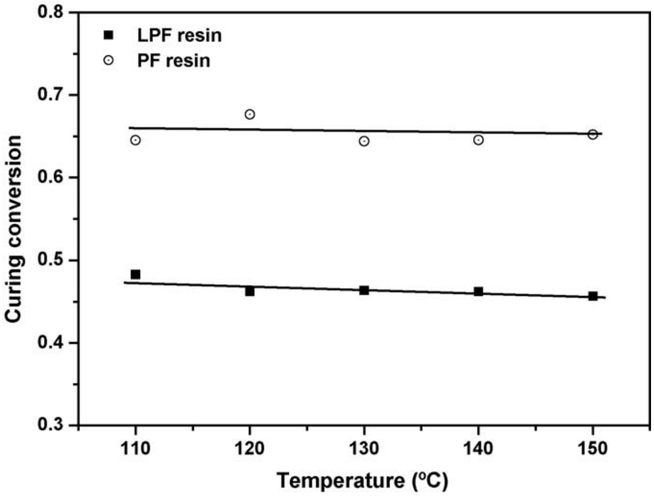

Fig. 1. DSC curing of gelated resol resins by TMA at different temperatures.

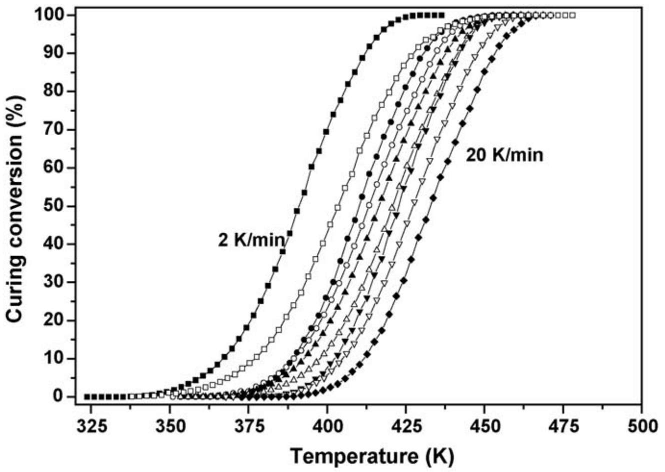

Fig. 2. Curing degrees of phenolic resin vs. temperature.

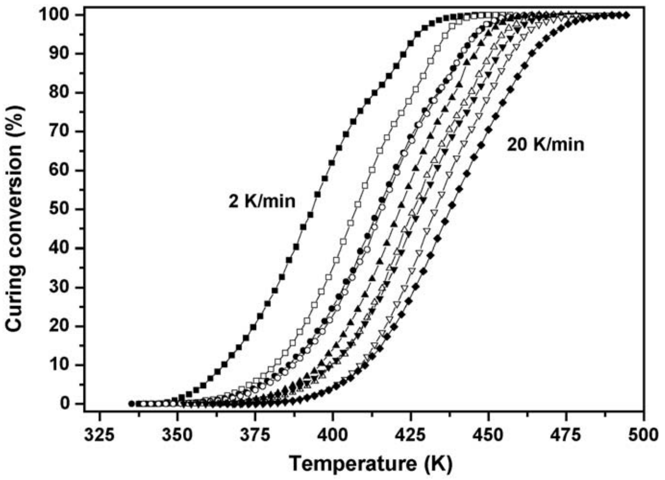

Fig. 3. Curing degrees of lignin–phenolic resin vs. temperature.

employed. The value obtained for α_{gel} is of 47 and 65% for the phenolic and lignin–phenolic resol resins, respectively, as shown in Fig. 1. This fact allows it to be considered that the gelation, in both resins, can be assimilated to an isoconversional principle.

Several authors have determined the α_{gel} value by different thermal analysis techniques to validate the isoconversional principle [25–27]. In some epoxy systems, it was found that the α_{gel} values vary between 52 and 58% [28,29] while unsaturated polyester presented α_{gel} values around 5% [erratum].

4.2. Curing kinetics

Figs. 2 and 3 display the curves of conversion degree against temperature for phenolic and lignin–phenolic resins, respectively. The data figures were applied to isoconversional methods of Ozawa, Kissinger–Akahira–Sunose, and Friedman to determine the kinetic parameters of resins curing process.

In the Ozawa isoconversional method, Eq. (5) is applied to different degrees of conversion of cured resins. According to this equation, for each conversion degree, the logarithm of the heating rate is correlated with the inverse of temperature. For a given heating rate, the temperatures at different curing degrees are obtained from the curves α-T, determined by dynamic DSC runs for each of the resins (Figs. 2 and 3). The values obtained for the activation energy and the constants A' of both resins by Ozawa's method are shown in Table 1. In most cases, correlation coefficients (R^2) are between 0.98 and 1. It can also be observed that the activation energy changes with the curing degree. Thus, the activation energy, in both resins, begins to increase slightly, then tends to be constant ($\alpha = 50$–60%) and finally rises again. This last increase could be explained as changes in reaction mechanism during the resin curing. Cure mechanism of phenolic resins is based on two reaction types [3]. First, addition reactions of hydroxymethyl groups to *ortho*- and *para*-free positions of phenol (or/and lignin in the case of lignin–phenolic resin). Second, condensation reactions of methylol phenols with phenol and/or methylol phenols (or/and methylol lignins in the case of LPF resins) lead to the desired resol. These reactions were experimentally confirmed by the obtained thermograms of the resins (Fig. 4a), where two peaks are exhibited. Thus, the

Table 1
Kinetic parameters of resins' curing determined by Ozawa's isoconversional method

α (%)	LPF resin				PF resin			
	A'	E (kJ/mol)	R^2	S.D.[a]	A'	E (kJ/mol)	R^2	S.D.[a]
2	707.54	2258.2	0.997	1.885	9.46	58.42	0.973	0.079
10	9.80	63.33	0.989	0.050	9.54	61.42	0.984	0.059
20	10.23	67.80	0.995	0.035	9.71	64.25	0.992	0.044
30	10.67	71.93	0.994	0.037	9.88	66.61	0.992	0.042
40	10.93	74.76	0.992	0.042	10.32	70.80	0.993	0.039
50	11.02	76.20	0.995	0.035	10.48	72.90	0.990	0.049
60	11.13	77.95	0.994	0.037	10.36	72.90	0.990	0.049
70	11.20	79.37	0.994	0.038	10.60	75.84	0.993	0.040
80	11.28	80.99	0.987	0.054	11.18	81.71	0.994	0.038
90	11.87	86.90	0.990	0.048	12.07	90.30	0.990	0.047
95	11.62	85.70	0.993	0.041	11.68	88.05	0.986	0.057
98	11.94	89.07	0.991	0.046	11.18	84.79	0.983	0.062
100	11.72	89.74	0.959	0.105	11.23	88.61	0.948	0.099

$A = [\log(k_0 E/g(\alpha)R) - 2.315]$.

[a] S.D.: standard deviation.

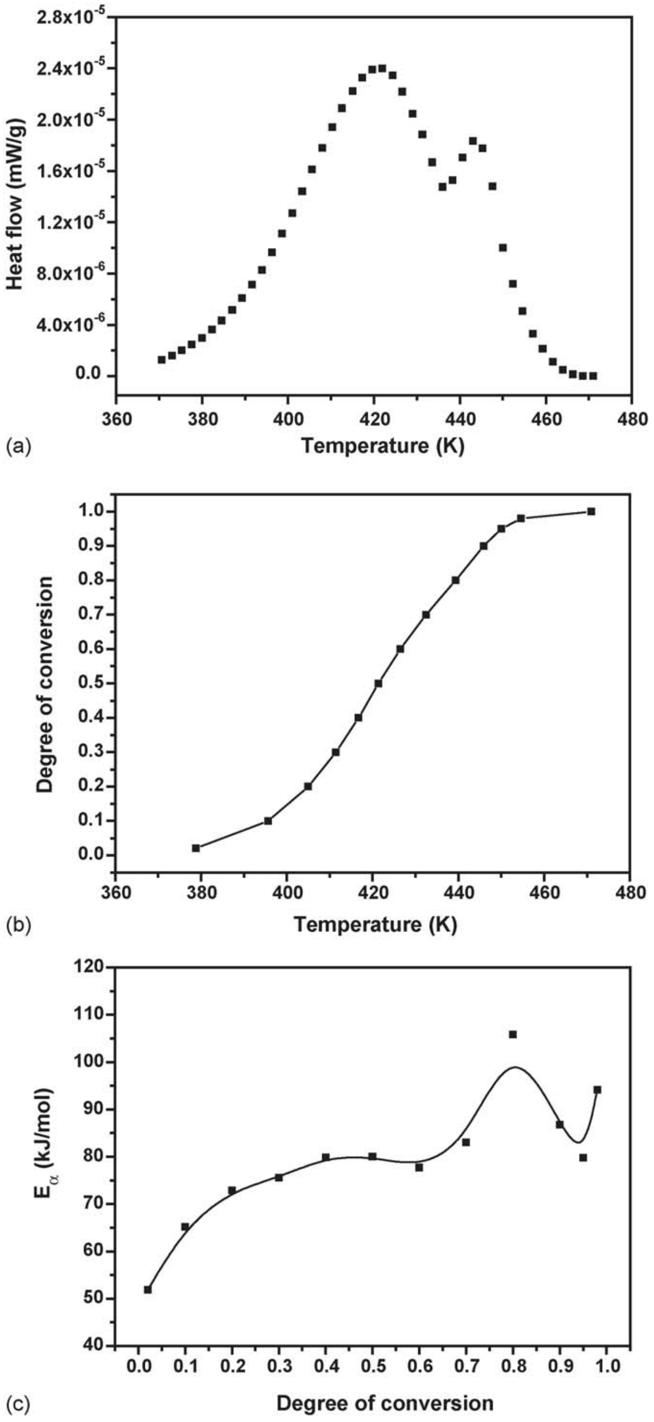

Fig. 4. Phenolic resol curing. (a) Typical thermogram by DSC ($\beta = 10\,^{\circ}\mathrm{C/min}$), (b) degree of conversion vs. temperature curve, (c) dependence of E_α on the curing degree.

peak first suggests addition reactions dominant the initial cure step, which is displayed through an important increase in the activation energy of the process (Fig. 4c) and low degree of conversion ∼30–40% (Fig. 4b). Following curing process, addition and condensation reactions occur simultaneously but the second step (condensation) is predominant while the first one starts to decrease. Therefore, an increase in activation energy is observed up to ∼80% curing degree. Later, the curve takes on a downward convex shape as a result of the transition in the control of kinetics from chemical reaction to diffusion control [30].

In addition, the activation energy value of LPF resin for a 2% cure degree is deviated with respect to the other results, as shown in Table 1. This deviation may be a result of the thermogram curvature, which is less than that of PF commercial resin. Thus, when the partial heat is found in a thermogram curve that has a height of less than 5% in relation to height of maximum peak temperature, kinetic parameters values with a significant error arise [31,32]. In short, in the average value of activation energies of the curing LPF resin the datum corresponding to $\alpha = 2\%$ has been rejected. The average values of activation energy for curing processes are 78.6 and 75.1 kJ/mol for the LPF and PF resins, respectively.

The results obtained with both resins before fitting the data to Kissinger–Akahira–Sunose's isoconversional method (Eq. (7)) are shown in Table 2. The correlation coefficient (R^2) values are close to those of the Ozawa's isoconversional method. The evolution of activation energy with the cure degree of both resins shows a similar trend to the results from the above mentioned method. Thus, the average values of the activation energy of LPF and PF curing processes are 71.9 and 70.7 kJ/mol, respectively. The standard deviation of these data is lower than 2%, which is also in agreement with the results obtained by the application of Ozawa's isoconversional method.

In the Friedman's isoconversional method, for each conversion degree, the logarithm of the heating rate is correlated with the inverse of temperature (Eq. (9)). This isoconversional method is different from the others because in this case, for a given temperature, the reaction rates ($r = \mathrm{d}\alpha/\mathrm{d}t$) at different curing degrees are obtained from the thermograms determined by dynamic DSC runs. However, the other methods directly correlate the curing degrees with the inverse temperature, which reduces error in the kinetic parameters calculated.

The results of the activation energy, logarithm of pre-exponential factor (A), and R^2 for both resins by Friedman's method are shown in Table 3. By using this 'isoconversional method,' the values of $\ln A$ are determined as a result of func-

Table 2
Kinetic parameters of resins curing determined by the Kissinger–Akahira–Sunose's isoconversional method

α (%)	LPF resin			PF resin		
	E (kJ/mol)	R^2	S.D.[a]	E (kJ/mol)	R^2	S.D.[a]
2	40.22	0.993	0.059	55.27	0.967	0.182
10	60.08	0.987	0.115	58.03	0.981	0.138
20	64.71	0.993	0.081	60.98	0.990	0.101
30	68.88	0.993	0.085	63.41	0.991	0.097
40	71.89	0.991	0.096	67.61	0.992	0.089
50	73.29	0.994	0.079	69.71	0.988	0.110
60	75.09	0.993	0.084	69.76	0.988	0.110
70	76.53	0.992	0.088	72.72	0.991	0.093
80	78.24	0.985	0.124	78.77	0.992	0.089
90	84.38	0.988	0.110	86.79	0.993	0.108
95	83.04	0.991	0.094	84.39	0.986	0.130
98	86.35	0.989	0.106	81.08	0.981	0.148

[a] S.D.: standard deviation.

Table 3
Kinetic parameters of resins curing determined by Friedman's isoconversional method

α (%)	LPF resin				PF resin			
	E (kJ/mol)	$\ln A$[a]	R^2	S.D.[b]	E (kJ/mol)	$\ln A$[a]	R^2	S.D.[b]
2	73.60	10.96	0.970	0.212	51.82	3.96	0.948	0.215
10	82.31	14.09	0.976	0.165	65.15	8.51	0.973	0.186
20	86.07	15.30	0.984	0.128	72.86	10.83	0.980	0.171
30	90.50	16.64	0.978	0.146	75.58	11.52	0.978	0.178
40	90.80	16.68	0.976	0.153	79.90	12.61	0.980	0.172
50	92.33	16.34	0.990	0.100	80.07	12.39	0.974	0.187
60	96.22	17.10	0.983	0.132	77.69	11.36	0.973	0.187
70	101.60	19.43	0.985	0.122	82.98	12.34	0.977	0.179
80	109.76	19.99	0.979	0.161	105.86	18.13	0.983	0.177
90	132.17	27.73	0.961	0.180	86.82	12.48	0.966	0.201
95	103.26	19.79	0.973	0133	79.77	9.85	0.933	0.269
98	167.39	33.04	0.989	0.122	94.12	12.83	0.929	0.291

[a] $\ln A_\alpha = C - f(\alpha_i)$, where $C = E/RT$ in Eq. (9).

[b] S.D.: standard deviation.

tion $f(\alpha)$, which is substituted by first order expression ($n=1$) [33]. The R^2 values obtained for the LPF and PF resins indicate a suitable fit for their respective kinetic parameters. Even so, the fits are not as satisfactory as in the case of the Ozawa and Kissinger–Akahira–Sunose's isoconversional method. This fact may be due to the error associated with the calculation of reaction rate ($d\alpha/dt$) from Eq. (10) and/or the chosen function to describe the resin curing process. In this case, determination of the baseline does not present any inconvenience; therefore, unsatisfactory fits in relation to the other methods is caused by the function chosen. The average values of activation energy are 92.6 and 79.4 kJ/mol for the LPF and PF resins, respectively (Table 3). The activation energy values of curing process for both resol resins begin to decrease for a conversion degree of 90%. However, this behavior cannot be detected by the Ozawa's isoconversional method. Although it is taken into account, the activation energy values are different from the usual trend and show dispersion in relation to the data obtained by the other methods, Ozawa and Kissinger–Akahira–Sunose model-free kinetics. This deviation, shown overcoat in the LPF resin, is due to the calculation of '*r*,' as was above mentioned, and to its low homogeneity with respect to the commercial PF resol resin. Note that phenolic resin is the result of a step-growth polymeration reaction, where phenol is linked together via methylene bridges. However, lignin–phenolic presents heterogeneity relative to commercial resin due to lignin incorporated and crosslinked with phenol, which has a complex structure [34,35].

From the dependence of the E on reaction extent it may be concluded that the reaction under consideration is a typical complex multi-step reaction. Although the system studied is complex, the results can be fitted to a function of reaction order $n=1$ like a first approach, as shown in Table 3. Thus, Fig. 5 shows the linear relationship between the logarithm of the pre-exponential factors and the activation energies of both resins during their curing processes. In addition, it is observed that all of the kinetic data are grouped into compensation curves of the type:

$$\ln A = aE + b \qquad (13)$$

where '*a*' is a constant and '*b*' is independent of temperature, the reaction rate, and the function $f(\alpha)$. As can be seen, the fit of kinetic parameters of the LPF and PF resins to this linear relationship is suitable. This can be explained by a compensation effect or isokinetic relationship between the activation energy and the pre-exponential factor. Therefore, high activation energies with low pre-exponential factors can describe the same kinetics as low activation energies with high pre-exponential factors [36–38]. However, it is not clear what the origin of these compensation effects are. It may be a results of changes in the sample, be an indicator of a complex process during the cured, or even may be a computational artifact [39–41]. Thus, experimental results obtained must be analyzed carefully to avoid a wrong interpretation.

In short, the results obtained with the Friedman's expression and with the Ozawa and Kissinger–Akahira–Sunose isoconversional methods reveal some differences. For instance, the activation energy values are always higher in Friedman's method. Although the R^2 of the fits of the three methods are suitable,

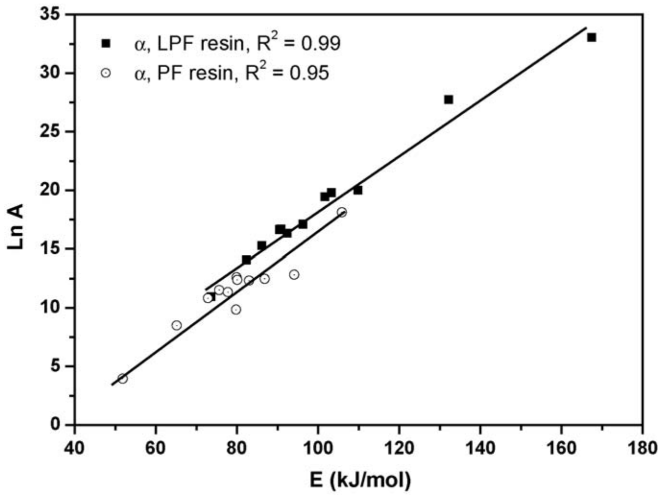

Fig. 5. ln *A* vs. *E* for each curing degree for phenolic and lignin–phenolic resins curing.

Friedman's isoconversional method shows different tendency in relation to the others. However, this method allows determining the activation energy as the pre-exponential factor. In order to make a correct comparison of the kinetic data we must take into account that the activation energy and the pre-exponential factor are two non-independent parameters, linked by the Arrhenius equation, and that they therefore cannot be discussed separately.

The Ozawa and Kissinger–Akahira–Sunose model-free describe similar evolution of the activation energy to the curing degree. The main advantage of Ozawa's isoconversional method is the chance to determine the kinetic constants of curing process without knowing the function $f(\alpha)$. In addition, the results obtained in this method can be used to predict the kinetic parameters of resins' isothermal curing process.

5. Conclusions

It is possible to establish that the cure of lignin–phenolic and phenolic resol resins studied complies with the isoconversional principle. This behavior has been verified experimentally by the TMA technique. The degree of conversion (α_{gel}) is determined by postcuring in a DSC of the resin gelled in TMA. The α_{gel} values are 47 and 65% for the LPF and PF resins, respectively.

The isoconversional methods can be applied to study the curing process of these polymers. Thus, the experimental results exhibit the dependence of activation energy on the curing degree of the phenolic and lignin–phenolic resins. In addition, in the three kinetic methods assayed, the variation of the activation energy at different curing degrees displays similar tendencies in both resins. In spite of the similarity of the results, the LPF resin shows a slightly lower average activation energy value than that of commercial PF resin. In addition, the parameters E and $\ln A$ in the Friedman's method show apparent compensation trends, which are necessary to explore the source of this behavior.

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