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Determination of curing kinetic parameters of lignin–phenol–formaldehyde resol resins by several dynamic differential scanning calorimetry methods

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Abstract

The curing kinetics of lignin–phenol–formaldehyde (LPF) and phenol–formaldehyde (PF) resol resins was studied by non-isothermal differential scanning calorimetry (DSC) at different heating rates. The data were fitted by means of the Borchardt–Daniels, Ozawa and Kissinger methods, which allow determining the kinetic parameters of both resins. The kinetic study has been realized to evaluate the effect of methylolated ammonium lignin sulfonate in the curing process of the lignin–phenolic resins. The results showed a slightly higher activation energy for LPF resin. It is attributed to the presence of modified lignosulfonate in this case. The obtained data, similar in both resins, indicate that the phenol can be replaced partially by a modified lignosulfonate in the phenolic resins.

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1. Introduction

Phenolic resins are thermosetting polymers which are very important and widely used in many applications. One of the possible applications of phenol–formaldehyde (PF) resol resins is in the board production [1,2]. These resins have good properties, but they present a noticeable price. So that way to reduce these prices is a partial replacement of phenol by fillers or extenders. A good candidate as phenol substitute is the lignin. This by-product of pulp industry is a renewable polymer and has a polyphenolic structure very similar to that of phenolic resin.

In this field, the partial replacement of phenol by non-modified lignin has been studied with different species of lignins: kraft, organosolv and lignosulfonates. Although the lignosulfonates have low reactivity by their higher molecular weight in relation to Kraft and Organosolv lignins, their availability and price are better. Among the usual lignosulfonates, ammonium species has been reported to be the most adequate to formulate PF resins [3,4]. The mean reasons are following: the phenolic resins with incorporation of ammonium lignosulfonates have better properties than the use of calcium or sodium lignosulfonates [5]. Besides, ammonium lignosulfonate is soluble in organic solvents, whereas the calcium, magnesium and sodium salts are only soluble in water. However, there are some authors that employ the calcium lignosulfonates owing to they are, in general, cheaper than the others [4,5].

Lignin has a low reactivity with respect to phenol because it has less reactive sites for reacting with the formaldehyde [6–8]. So that, it is needed to modify its structure to obtain a polymer with more reactive functional groups. The lignin can be modified by different methods, such as: methylolation, phenolation, demethylation [9,10]. In this research, lignosulfonate was modified by methylolation because of the reaction is carried out in the same alkaline medium that the formulation of resol resins. The works realized with modified lignins for the formulation of lignin–resol resins shown that, in general, these resins have better properties

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than that of resins synthetized with non-modified lignin [11,12]. In any case, the formulation of phenolic resins is well known [12–16]. However, the curing kinetics of phenol–formaldehyde resins has been less studied. It is known that the properties of the cured resin depends on its composition but, in addition, they are markedly dependent on the extent of cure. It is important to study the cure process of phenolic resins in order to obtain a better knowledge of polymer for its final application.

Differential scanning calorimetry (DSC) has been used to analyze the cure process of these thermosetting polymers. This technique is a good tool to follow the polymers curing kinetics because it not only isolates the temperature-dependent behavior for a given chemical process, besides it allows to determine the heat associated to the cure process as a function of temperature [17].

The methods used to study the cure kinetics can be classified into mechanistic or phenomenological. 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 [18].

The main empirical models to obtain kinetic information from DSC dynamic runs can be divided in three groups. The first is highly attractive because with a single scan it gives enough information to determine all kinetic parameters. The second technique is based on the variation of the exotherm peak temperature with heating rate, and the third method requires, as the second one, at least three heating rates, and analyzes the influence of the temperature to reach a constant conversion on the heating rate.

The aim of the present work is to determine by DSC the cure thermochemical parameters of lignin–phenol–formaldehyde (LPF) and commercial phenol–formaldehyde resins. The results of LPF resin curing process were compared with those obtained with a commercial PF resin (reference sample). This comparison is interesting to evaluate the possibility of the phenol partial replacement in the phenolic resins by a methylolated softwood ammonium lignosulfonate.

2. Experimental

2.1. Materials

Phenolic commercial resol resin tested was supplied from Bakelite Ibérica (Spain). This product is obtained by the polymerization between phenol and formaldehyde in an alkaline medium. LPF resin was synthesized in laboratory with a methylolated softwood ammonium lignosulfonate. The methylolation conditions were reported in a previous work [23]. First, methylolated lignosulfonate, phenol and sodium hydroxide were dissolved in 60 ml of water and heated to 80 °C. Then, the formaldehyde was added in six equal shares at intervals of 15 min. The reaction time was fixed in 5 h. Finally, the resin was distilled in order to adjust both its water content and its viscosity. The formaldehyde/phenol-modified lignosulfonate (F/PL) and sodium hydroxide/phenol-modified lignosulfonate (S/PL) molar ratios were 2.6 and 0.6, respectively. The content of modified ammonium lignosulfonate was fixed in 35% (w/w).

2.2. DSC measurements

The calorimetric measurements of both resins (PF and LPF) were performed on a Mettler Toledo DSC 821^{e} calorimeter using pressure medium pans (ME-26929). The pans, with a volume of 120 μl, can withstand vapor pressures up to 10 MPa. Since the difficulty to weight in all cases the same amount of sample, the different thermograms were normalized, by the calorimeter, at 1 g. Later, the baseline “spline” was subtracted from the original thermogram. Thus, it is possible to calculate the total and partial heats, the cure degree and the reaction rate of both resins curing processes. The Borchardt–Daniels’ method was applied with nine heating rates (2, 4, 6, 8, 10, 12, 14, 16, and 20 °C min^{-1}) in a scanning temperature range from 30 to 250 °C. These runs were also employed for the multi-heating rate methods of Ozawa and Kissinger.

2.3. Kinetic methods

In general, the kinetic models of thermoset polymer are based on a single step kinetic Eq. (1) that relates the curing evolution ($\mathrm{d}\alpha/\mathrm{d}t$) at constant temperature with some function of the reactants concentration, $f(\alpha)$, through a rate constant k. The rate equation can be expressed as follows:

$$r = \frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(T)\,f(\alpha) \tag{1}$$

where r is the reaction rate, t the time, α the degree of conversion, $k(T)$ the rate constant that depends on temperature according to Arrhenius law, and $f(\alpha)$ is a function, which depends on kinetic model applied.

The heat flow data calculated using the area under the exotherm peak were utilized to obtain the degree of conversion (α) and the reaction rate ($\mathrm{d}\alpha/\mathrm{d}t$). The degree of conversion can be written by the following expression:

$$\alpha = \frac{(\Delta H_{\mathrm{p}})_t}{\Delta H_0} \tag{2}$$

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

The kinetics of the curing process is proportional to the measured heat flow and it can be described as:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \frac{\mathrm{d}H/\mathrm{d}t}{\Delta H_0} \tag{3}$$

where $\mathrm{d}H/\mathrm{d}t$ is the peak height under the curve at temperature T.

The kinetic parameters of thermosetting polymers cure were calculated by Borchardt and Daniels method [19]. This model, based on a single-heating rate run to analyze the curing reaction assuming n^{th} order kinetics, is expressed by Eq. (4).

$$\ln\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right) = \ln k_0 - \frac{E}{RT} + n\ln(1-\alpha) \tag{4}$$

This equation can be solved to obtain the parameters (k_0, E, and n) by multiple linear regression. The method is interesting because it provides enough information with a single dynamic experiment by DSC. However, the results obtained for the cure thermoset usually overestimate the value of the kinetic parameters with respect to isothermal data.

Other non-isothermal methods, more accurate to determine the curing kinetic parameters, are carried out at different heating rates. These methods start with the integral form of the process rate equation, which can be expressed as follows:

$$\int_{\alpha_0}^{\alpha_p} \frac{\mathrm{d}\alpha}{f(\alpha)} = \frac{k_0}{\beta}\int_{T_i}^{T_p} \mathrm{e}^{-E/RT}\,\mathrm{d}T \cong \frac{k_0 E}{\beta R} P\left(\frac{E}{RT}\right) \tag{5}$$

The polynomial function $P(E/RT)$ can be calculated according to the Doyle's approximation [20]:

$$\log\left[P\left(\frac{E}{RT}\right)\right] = -2.315 - 0.4567\left(\frac{E}{RT}\right) \tag{6}$$

which is valid for an E/RT included between 60 and 20. Eqs. (5) and (6) may be combined and rearranged as:

$$\log\beta = -2.315 - 0.4567\left(\frac{E}{RT_{\mathrm{p}}}\right) + \log\left(\frac{k_0 E}{R}\right) - \log F(\alpha) \tag{7}$$

where $F(\alpha)$ is a constant function, described as:

$$F(\alpha) = \int_{\alpha_0}^{\alpha_p} \frac{1}{f(\alpha)}\mathrm{d}\alpha \tag{8}$$

Ozawa's method is based on a linear relationship between the logarithm of the resin heating rate and the inverse of the peak temperature (Eq. (7)) [21]. Therefore, the curing activation energy can be determined from the resultant slope. Kissinger suggests a similar method, which relates the logarithm of (β/T_{p}^2) with the inverse of the peak temperature [22], through the following expression:

$$-\ln\left(\frac{\beta}{T_{\mathrm{p}}^2}\right) = \frac{E}{RT_{\mathrm{p}}} - \ln\left(\frac{k_0 R}{E}\right) \tag{9}$$

The graphic representation of Eq. (9) allows to determine both the activation energy and the pre-exponential factor of curing kinetics.

3. Results and discussion

The thermograms of the PF and LPF resins at different heating rates are shown in Fig. 1. In the thermograms of both resins can be observed two peaks. The first appears at lower temperature (T_{p1}) and it is the result of the free formaldehyde in the resin, which can lead to a different product. The second peak (T_{p2}) is due to condensation reactions among the phenol and the formaldehyde, and the methylolated lignosulfonate in the LPF case [4]. The peak temperatures of LPF resin are lesser than that of PF resin (Table 1) and they might be a consequence of peak broadening [4], but this fact not imply that the cure process of LPF resin can be faster than that of the commercial PF resin.

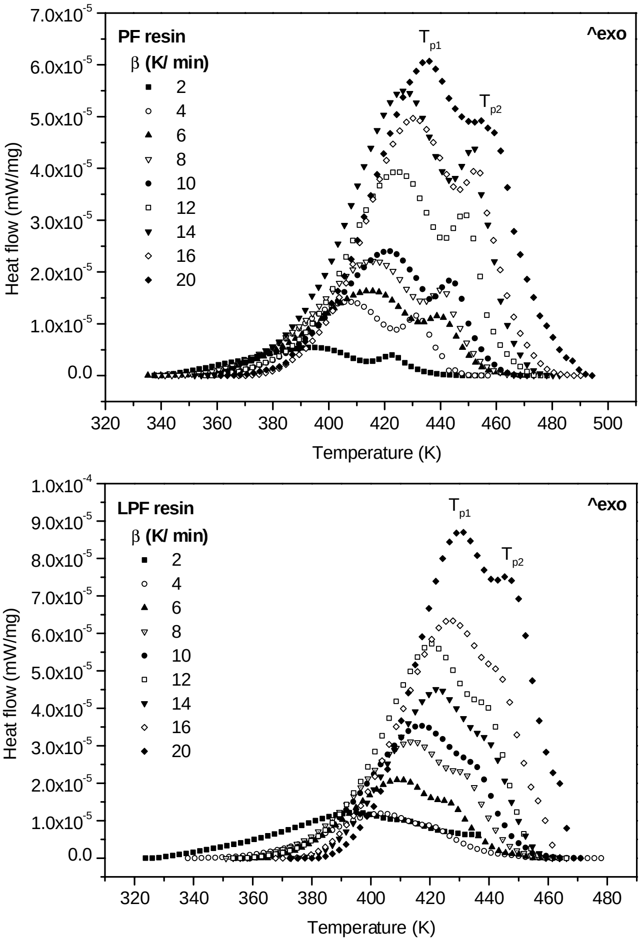

Fig. 1. DSC thermograms of PF and LPF resol resins.

In order to obtain the kinetic parameters, the data plotted in the Fig. 1 have been treated by the methods described above. Although the Borchardt–Daniels' method is based on the performance of a single scan by DSC, in the present work nine scans were performed at different heating rates. Non-linear regression was used to fit experimental data to the expression of the proposed model [24]. So that, it is necessary to determine reaction rate, total heat, partial heats and resin cure degree. In the Table 1 are shown the data of the reaction heats for the PF and LPF resins according to vary the heating rate employed. The reaction exothermic of the LPF systems seems to decrease with heating rate, while that of the PF systems remains constant. This fact

Table 1
Peaks temperatures and reaction heats of curing process of both resins at different heating rates

β (K min^{-1})	LPF resin				PF resin			
	T_{p1} (K)	T_{p2} (K)	ΔH_0 (J g^{-1})	ΔH_0[a] (J mol^{-1})	T_{p1} (K)	T_{p2} (K)	ΔH_0 (J g^{-1})	ΔH_0[a] (J mol^{-1})
2	395	–	108.4	3252	392.7	422.6	118.0	3540
4	401	419.6	113.6	3408	408	431	116.9	3507
6	411	427.2	83.6	2508	415.7	438.7	122.9	3687
8	413.4	430.2	84.4	2532	415.8	439.8	131.7	3951
10	417.3	433.6	81.1	2433	422	443	100.0	3000
12	420.6	439.5	63.4	1902	425.4	449.4	98.0	2940
14	422	440.6	64.7	1941	426.6	452.3	121.9	3657
16	427.8	442.2	76.7	2301	430.2	454.2	102.2	3066
20	431.3	445.3	52.0	1560	436	457	123.2	3696

[a] Heat of polymerization per mole of formaldehyde group.

should be explained by the presence of lignosulphonate in the LPF that makes it less homogeneous and reactive than commercial resin. Before non-linear fit, a multiple regression in each one of the obtained thermograms at different heating rates was applied. This previous fit allowed calculating the initial values of $\ln k_0$, E/R and n, which were employed to start the successive iterations associated to the non-linear fit.

Table 2
Kinetic parameters of PF and LPF resol resins cure determined by Borchardt–Daniels' model application

β (K min^{-1})	Parameters[a]	LPF resin		PF resin	
		Value ± standard error	R^2	Value ± standard error	R^2
2	$\ln \mathrm{k}_0$	4.15 ± 1.16	0.844	10.74 ± 1.64	0.919
	E/R	6 000.21 ± 420.67		8 681.01 ± 614.55	
	n	0.32 ± 0.04		1.17 ± 0.05	
4	$\ln k_0$	16.08 ± 1.27	0.938	17.67 ± 1.37	0.945
	E/R	10 828.04 ± 480.61		11 395.10 ± 523.69	
	n	1.16 ± 0.04		1.16 ± 0.04	
6	$\ln k_0$	32.67 ± 4.25	0.756	14.05 ± 1.02	0.933
	E/R	17 444.02 ± 1654.53		10 139.48 ± 389.13	
	n	1.36 ± 0.14		1.02 ± 0.04	
8	$\ln k_0$	20.64 ± 2.31	0.864	18.96 ± 1.87	0.853
	E/R	12 614.31 ± 901.21		12 014.44 ± 713.81	
	n	0.98 ± 0.06		1.04 ± 0.08	
10	$\ln k_0$	19.53 ± 1.59	0.926	16.07 ± 1.12	0.952
	E/R	12 181.25 ± 630.78		11 022.37 ± 443.94	
	n	0.99 ± 0.04		0.96 ± 0.03	
12	$\ln k_0$	24.32 ± 1.59	0.930	17.06 ± 1.01	0.952
	E/R	14 045.77 ± 627.20		11 344.52 ± 400.44	
	n	1.02 ± 0.05		0.98 ± 0.03	
14	$\ln k_0$	25.15 ± 3.34	0.828	17.66 ± 1.26	0.925
	E/R	14 707.05 ± 1355.78		11 454.45 ± 499.29	
	n	0.96 ± 0.07		1.02 ± 0.04	
16	$\ln k_0$	34.83 ± 4.83	0.728	25.34 ± 2.19	0.873
	E/R	18 580.58 ± 1938.06		14 932.94 ± 889.72	
	n	1.23 ± 0.19		1.17 ± 0.07	
20	$\ln k_0$	45.31 ± 5.22	0.778	21.41 ± 1.78	0.867
	E/R	23 087.78 ± 2119.54		13 324.44 ± 723.46	
	n	1.49 ± 0.22		1.09 ± 0.07	
Average value	$\ln k_0$	24.74 ± 2.74	0.853	17.66 ± 1.47	0.913
	E/R	14 343.00 ± 1084.02		11 589.86 ± 577.56	
	n	1.10 ± 0.01		1.07 ± 0.05	

[a] k_0 in s^{-1}; E/R in K.

The kinetic parameters (E, k_0 and n) calculated for the curing reactions of LPF and commercial PF resins from Borchardt–Daniels' method can be seen in Table 2. Data from Table 2 show that the results with heating rates of 2 and 20 K min^{-1} are deviated with respect to the remaining values. The behavior at $\beta = 2\,\mathrm{K\,min^{-1}}$ is produced by the thermal decomposition of LPF resin, which probably interferes with the later stages of its cure. The opposite case, $\beta = 20\,\mathrm{K\,min^{-1}}$, is explained by the fast heating rate, which produces a resin partial cure [25,26]. This fact is evident because there is a diminution of the curing exotherm heat. So that, these runs were omitted to calculate average values of kinetic parameters of both resins.

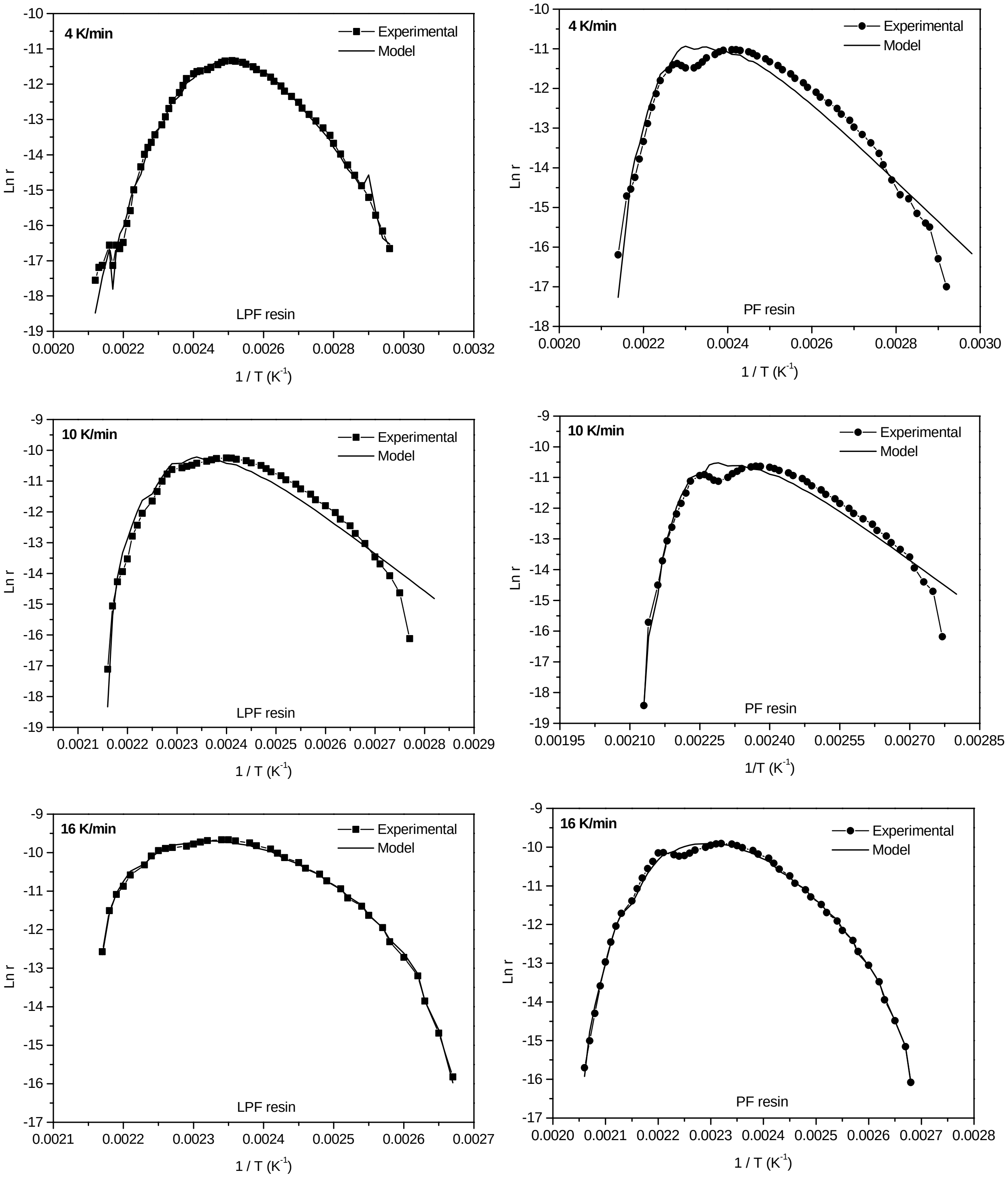

Fig. 2. Comparison among the experimental and the simulation data for LPF and PF resol resins.

In the Fig. 2, where curing rate versus inverse temperature is represented, is compared the curing experimental data with the simulated values obtained from the Borchardt–Daniels' model application. As can be seen, the predicted values are in good agreement with those obtained by DSC. The activation energy (E) of PF and LPF resins is 96.3 and 119.2 kJ mol^{-1}, respectively (Table 2). The data of the commercial resin have a better fit than that of the lignin–phenol–formaldehyde resin. Both resins have similar reaction orders, which are in agreement with the values reported by other authors [27–29].

While the Borchardt–Daniels' method employs a single run, Ozawa and Kissinger's model are not longer so. These methods utilize simultaneously several heating rates [21,30]. The data of the heating rate (β) and the peak temperature (T_{p1}) used in the linear fit of these models for lignin–phenolic resol and commercial phenolic resins are shown in the Table 1. The activation energies obtained in the Ozawa's method for both resins, LPF and PF, are 77.7 and 77.1 kJ mol^{-1}, respectively. These results are according to the literature on other polymers such as epoxi, epoxi-amine and unsaturated polyester resins [31,32].

In the case of Kissinger's method, the activation energies of LPF and PF resins are 74.8 and 74.2 kJ mol^{-1}, respectively. The R^2 calculated is the same in both cases: 0.992. These results are also according to the literature concerning to the epoxi resins [32]. Ozawa and Kissinger's methods give a similar activation energy for formulated and commercial resins. The deviation of activation energies between both methods is lower than 4%. The error associated with these models depends on the selected baseline to calculate the peak temperature.

At first the higher activation energy of the lignin–phenolic resol in the Borchardt–Daniels' method could be explained by the lower reactivity of the methylolated lignosulfonate incorporated in its formulation compared with that of phenol. It is undeniable that the phenol structure presents more reactive sites than the aromatic rings of modified lignosulfonate. Hence, the content of methylol groups cross-linked should be larger in the phenolic resins. However, the results obtained in the others methods are as similar that do not allow affirming this difference possible between the reactivity of both resins.

The three methods studied have the same disadvantage: they give a single value of the activation energy for the overall process, when in a complex system, as the phenolic resins, this parameter changes with the curing time. As a result, the activation energy variations associated with their complex kinetics could not be revealed by these methods. However, the Ozawa and Kissinger's methods are suitable to apply them in the thermosetting resins because of these models are not affected significantly by the baseline shift. Besides, these methods include simplicity, applicability to many types of reactions and relative insensitivity to solvent effects and secondary reactions [33].

It is found that the activation energy determined by the Borchardt–Daniels' method is higher than those calculated by Ozawa and Kissinger's models. This overestimation of activation energy is according to literature [17] and it is due to the simplicity of Borchardt–Daniels' method, based on a single scan by DSC but it has as advantages its straightforward and rapid application to obtain a wide kinetic information.

4. Conclusions

The presence of methylolated ammonium lignosulfonates in the resol formulation gives rise to a diminution of its peak temperature, which does not obey to faster cure of these resins with respect to that of commercial PF resins. The peak temperature shift in the LPF resin responds to its bigger wide peak in relation to it observed in the PF resin thermograms.

The kinetic parameters of LPF and PF resins have been determined and the lignosulfonate effect on the curing process was analyzed by DSC technique. Although the Borchardt–Daniels' method is the most rapid of the three methods studied because with a single run is feasible to calculate the kinetic parameters, the activation energy is overestimated with respect to the energy (E) values established by Ozawa and Kissinger's models, which are more accurate.

The use of Bochardt–Daniels' method is justified when the reaction order and the pre-exponential factor (Ozawa method does not allow obtaining k_0) are required. The Bochardt–Daniels' method can be also justified when it is necessary to determine rapidly an approximated value of activation energy of resins curing process.

In any case, the obtained values for the activation energy and the reaction order of the curing process are similar in both resins. It indicates the viability of the partial replacement of phenol by methylolated softwood ammonium lignosulfonate in the formulation of the resol phenolic resins.

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