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Isoconversional kinetic analysis of novolac-type lignophenolic resins cure

A. Tejado[a], G. Kortaberria[a], J. Labidi[a], J.M. Echeverria[b], I. Mondragon[a,*]

[a] Materials + Technologies Group, Chemical & Environmental Engineering Department, University of the Basque Country (UPV/EHU),
Pza. Europa 1, 20018 Donostia-San Sebastián, Spain
[b] Hexion Ibérica S.A., Epele 39, Ctra a Navarra, 20120 Hernani, Spain

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ABSTRACT

Several phenomenological models (including simple models by Ozawa and Kissinger and the Kissinger–Akahira–Sunose isoconversional method) have been used to compare the cure kinetics of two lignin-based novolac-type phenolic resins with those from a commercial novolac system. When 45 wt% phenol is substituted by a sulfonated kraft lignin, an important reduction in the activation energy is obtained. This behaviour has been attributed to the incorporation of an extra amount of hydroxymethyl groups in the formulation, as they are present in important quantities in the original lignin structure. KAS isoconversional model shows that the rise in viscosity derived from lignin introduction leads to a moderate change in the limiting stage from a kinetic to a diffusion regime, while condensation reactions, which are favoured by the abundance of lignin hydroxymethyl groups, acquire high relevance in LPF-45 system cure. Finally, competition with other mechanisms initiated at high temperature is reported at high conversion grades for all cases.

1. Introduction

Phenolic (PF) resins were the first completely synthetic plastics to be created and, since then, they have acquired huge importance through their use in many applications in the automotive, construction, electric and aerospace industries. Among all applications, their use as adhesives in wood panel products, which is derived from their excellent bonding behaviour, is one of the most relevant. This application accounted for up to 55% of the whole PF consumption of the United States in the year 2000 [1].

Due to increasing environmental restrictions, in the last decades there has been a huge research initiative to reduce the relatively high formaldehyde emissions associated with these resins. A possibility that is receiving much attention is the introduction of lignin (L) in the resin formulation as a substitute for part of the petrochemical derived components. L is a polyphenolic macromolecule present in the cell wall of plants and is, with the exception of cellulose, the most abundant renewable natural resource on Earth. Depending on the original source and pulping method used for its extraction, physicochemical characteristics of L and thus its suitability in phenolic formulations vary noticeably [2].

Due to the fact that they are thermosetting systems, it is critically important to control the curing process of PF resins by which they are transformed from viscous liquids to elastic gels (gelation) and finally to glassy solids (vitrification). From an industrial point of view this is absolutely necessary for obtaining the desired final properties. The study of cure kinetics contributes to a better knowledge of the complex process governing the curing of PF resins and helps to improve the quality of final products.

Cure kinetics can be analyzed by using mechanistic or phenomenological models. Mechanistic models show more accuracy as they are based on the balance of all the species formed or consumed during the curing process. In the case of phenolic resins this is extremely complicated due to the high complexity of curing reactions, involving the formation of a great number of intermediate compounds such as benzoxazines, benzylamines, imines, amides, imides and many others [1,3–5]. Mechanistic models become even more complex when the resins to be analyzed are L-based. Phenomenological models based on empirical data are found to be more appropriate for these cases [6–8]. Among them, different methodologies can be used for the determination of cure kinetic parameters. Some direct methods, e.g., Borchardt–Daniels [9] employ a single dynamic differential scanning calorimetry (DSC) scan to calculate these parameters, while others like Ozawa [10,11] and Kissinger [12] models, use multiple dynamic scans with the same objective. Isoconversional models are another type of kinetic model and provide more accurate information as they evaluate the changes in the activation energy throughout the curing process. These models are especially interesting for studying the complex curing process of phenolic resins.

In this work, two simple phenomenological kinetic models (Ozawa and Kissinger) as well as an isoconversional model

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* Corresponding author. Tel.: +34 943 017271; fax: +34 943 017130.
E-mail address: inaki.mondragon@ehu.es (I. Mondragon).

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(Kissinger–Akahira–Sunose (KAS)) have been used to obtain kinetic parameters from the curing processes of two novolac-type L-based phenolic (LPF) resins, differing in L content, and a commercial novolac resin that was used as reference.

2. Theory: kinetic models

DSC technique is a very useful tool to study the kinetics of thermosetting resins [7,8,13–17], as it allows the calculation of kinetic parameters from the thermograms by relating the heat flow to the reaction rate.

The expression from which all phenomenological kinetic models are derived relates the reaction rate, $d\alpha/dt$, to a conversion function, $f(\alpha)$, through a reaction constant, $k(T)$, that is temperature-dependent:

$$\frac{d\alpha}{dt} = A \exp\left[\frac{-E_a}{RT}\right] f(\alpha) \tag{1}$$

with A the Arrhenius frequency factor, or pre-exponential factor, and E_a the activation energy per mol.

For non-isothermal conditions, when the temperature is raised at a constant heating rate (β) the integral form of the single step kinetic equation can be expressed as

$$g(\alpha) = \int_0^{\alpha} \frac{1}{f(\alpha)}\, d\alpha = \frac{A}{\beta} \int_{T_0}^{T} \exp\left[\frac{-E_a}{RT}\right] dT \tag{2}$$

As has been widely reported [7,10–12,18–20], the use of different approximations to solve the temperature integral give rise to Ozawa (Eq. (3)) and Kissinger (Eq. (4)) expressions where the activation energy is related to the heating rate and the temperature at the peak of the exothermic curve (T_p) observed by DSC.

$$-\ln\beta = 1.0516\left(\frac{E_a}{RT_p}\right) - A' \tag{3}$$

$$-\ln\left(\frac{\beta}{T_p^2}\right) = \frac{E_a}{RT_p} - \ln\left(\frac{A^1R}{E_a}\right) \tag{4}$$

A plot of $-\ln\beta$ *vs* $1/T_p$ or $-\ln(\beta/T_p^2)$ *vs* $1/T_p$ gives a straight line from which activation energy can be determined.

Isoconversional models are based on the assumption that the activation energy remains constant for a given conversion grade regardless of curing temperature. This aspect has been confirmed for the curing process of both PF [16,17] and LPF [7,21,22] resins. In this work, KAS model [23] has been used for the determination of kinetic parameters of LPF resins cure over the whole conversion range.

Conversion grade is defined as

$$\alpha = \frac{\Delta H_\alpha}{\Delta H_0} \tag{5}$$

where ΔH_α is the heat released at a given conversion value, corresponding in dynamic scans to a single temperature, and ΔH_0 the total heat released at the end of the reaction. Considering the expression described above for Kissinger simple model and using the definition of conversion as a function of the enthalpy (Eq. (5)), the following expression is obtained for KAS model:

$$-\ln\left(\frac{\beta}{T_\alpha^2}\right) = \frac{E_\alpha}{RT_\alpha} - \ln\left(\frac{A_\alpha^1R}{E_\alpha}\right) \tag{6}$$

For a given heating rate, each conversion grade is associated with a single temperature (T_α) and thus the corresponding activation energy (E_α) can be determined from the slope of the straight line obtained by plotting $-\ln(\beta/T_\alpha^2)$ *vs* $1/T_\alpha$ in the same way as for simple models.

3. Experimental

3.1. Materials

A sulfonated kraft L from mixed softwoods (Diwatex 40P) was kindly supplied by Basf Curtex and used without further purification; phenol (P), curing agent hexamethylenetetraamine (HMTA) and PF novolac used as reference were gifts from Hexion Specialty Chemicals Ibérica, while F (37 wt% aqueous solution) was supplied by Aldrich.

3.2. Resin preparation

Two novolac type LPF resins (LPF-25 and LPF-45) where P has been partially substituted by L at two different proportions (25 and 45 wt%) have been synthesized, as reported previously [24]. The procedure follows the typical scheme used for commercial PF in the industry, with a previous L–P mixing step in addition. Those prepolymers, as well as the reference PF resin, have been cured with 10 wt% of HMTA.

3.3. DSC measurements

DSC measurements were carried out in a Mettler Toledo DSC 821e module previously calibrated with high purity indium and zinc standards. Experiments were conducted in N_2 atmosphere, working with medium pressure pans and 5–10 mg samples. Runs at different heating rates (4, 8, 12, 16 and 20 °C/min) were performed in a temperature range from 30 to 300 °C, though Fig. 1 only shows the range at which the curing reaction takes place. Total released enthalpy (ΔH_0) and temperature at the peak of the exothermic curve (T_p) of the curing reactions were recorded.

4. Results and discussion

Fig. 1 shows the thermograms obtained by DSC for PF, LPF-25 and LPF-45 at different heating rates (4, 8, 12, 16 and 20 °C/min), while T_p values corresponding to these curves are reported in Table 1. These data have been used for the determination of cure kinetic parameters through the application of Ozawa and Kissinger simple models and, in a second approach, KAS isoconversional model. In all cases, correlation coefficients (R^2) higher than 0.99 have been obtained.

As seen in Fig. 1, both L-modified systems undergo their respective curing processes at lower temperatures compared to that of commercial PF. This behaviour reveals that the introduction of L in the formulation induces a positive effect, perhaps due to good accessibility of L reactive positions have as this compound is distributed homogeneously within the prepolymer. Peng and Riedl [25] reported a similar behaviour for a phenolic resin modified with 30 wt% of lignosulfonate which was attributed to a catalytic effect that this compound has over the curing process.

4.1. Ozawa and Kissinger simple models

Ozawa [10,11] and Kissinger [12] models have been used for the calculation of activation energies derived from the curing processes of PF, LPF-25 and LPF-45 resins. Those kinetic parameters have been determined representing $-\ln\beta$ *vs* $1/T_p$ (Ozawa model, Fig. 2) and $-\ln(\beta/T_p^2)$ *vs* $1/T_p$ (Kissinger model, Fig. 3) according to Eqs. (3) and (4). Results are reported in Table 2 and in all cases E_a values show good reproducibility.

As can be seen in Table 2, LPF system containing 25 wt% L shows an E_a value close to that of PF, while this parameter undergoes an important decrease when the substitution rises to 45 wt%. This

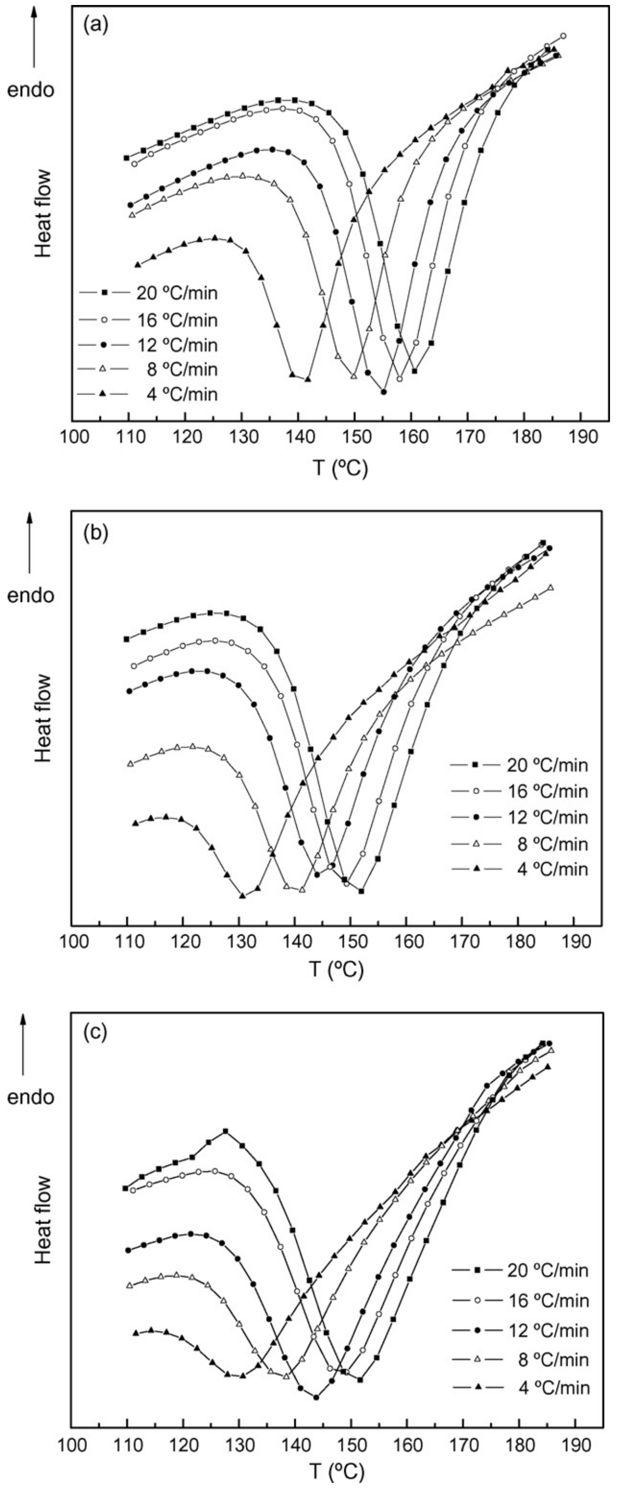

Fig. 1. DSC thermograms at different heating rates obtained for (a) PF, (b) LPF-25 and (c) LPF-45.

Table 1
Temperature at the maximum of the exothermic curve (T_p) for the different systems analyzed

β (°C/min)	T_p (°C)		
	PF	LPF-25	LPF-45
4	140.9	132.1	130.7
8	149.5	140.6	138.5
12	154.6	144.8	143.8
16	158.3	149.1	149.1
20	161.3	151.3	151.6

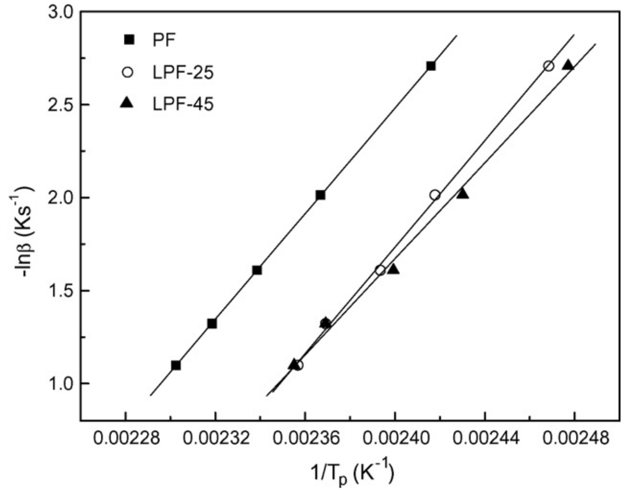

Fig. 2. $-\ln\beta$ *vs* $1/T_p$ plottings according to Ozawa model.

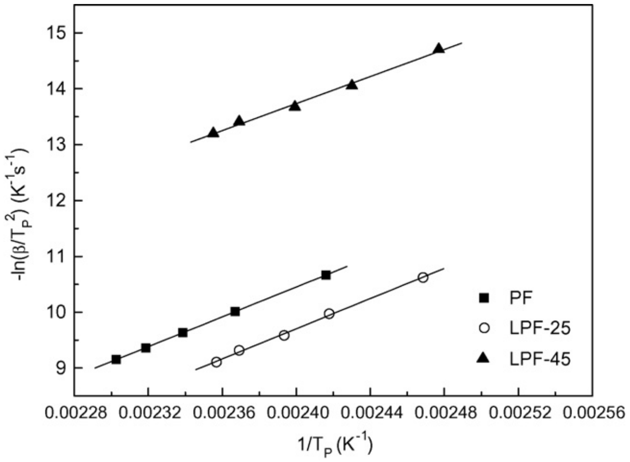

Fig. 3. $-\ln(\beta/T_p^2)$ *vs* $1/T_p$ plottings according to Kissinger model.

behaviour indicates that the curing process proceeds much easier in LPF-45 system. Gabilondo et al. [17] observed an important decrease in the E_a values for a resole resin when F/P molar ratio was set to high values, which they believed to be caused by an activation effect from the excess of $-CH_2OH$ groups over phenolic rings. This kind of group is also present in the original L structure and it is well known that it can react with the rest of the components in the formulation in the same way as $-CH_2OH$ groups in a conventional resole resin. Obtained results suggest that an important number of L hydroxymethyl groups have taken part in the curing reaction of LPF-45, making it proceed easier and, thus, reducing the activation energy required. LPF-25 would not show this behaviour because

Table 2
Activation energies and regression factors obtained with Ozawa and Kissinger simple models

	Ozawa		Kissinger	
	E_a (kJ/mol)	R^2	E_a (kJ/mol)	R^2
PF	112.1	0.999	110.9	0.999
LPF-25	113.0	0.998	112.0	0.998
LPF-45	102.0	0.994	100.3	0.994

most of hydroxymethyl groups incorporated with the L have probably reacted during prepolymer synthesis with highly reactive hydroxymethylphenol (HMP) species created in the initial steps of the polymerization. This reaction is favoured by the high P/L (and so HMP/L) proportion in the initial blend. On the other hand, this proportion is much lower and, at the same time, the quantity of L–CH_2OH groups much higher in the 45 wt% substituted system; as consequence, some of them can remain unreacted at the end of the synthesis.

Pérez [22] and Peña et al. [8] reported E_a values of 117 and 105 kJ/mol for non-modified novolac resins containing 9 and 10 wt% HMTA, respectively. These data are in the same range as the E_a determined in this work (112 kJ/mol). Dos Santos [26] studied the curing kinetics of a kraft L-modified novolac resins and obtained activation energy of 200 kJ/mol. However, this great difference is due to the fact that Borchardt–Daniels method tends to overestimate that parameter [20]. On the other hand, Pérez [22] determined that the substitution of 30 wt% of P with an ammonic lignosulfonate resulted in a decrease of the curing activation energy (104 kJ/mol), showing the same tendency reported in this work for the 45 wt% L-substituted resin.

4.2. KAS isoconversional model

Simple models are useful tools that allow studying the curing process of a thermosetting resin in a global manner, but they provide us with very little information on the evolution of such reactions. Related to this, isoconversional models analyze the curing processes in more detail as they determine a single activation energy for each conversion (E_α). These models have been successfully used for the kinetic analysis of several thermosetting resins [17,19,20,27–33]. Some of these works deal with lignosulfonate-modified resole [20–21] or novolac [22] resins, and reveal the validity of isoconversional principle in LPF resins.

Considering conversion grade as defined in Eq. (5) it is possible to use heat flow values determined by DSC to obtain the evolution of conversion with temperature. Fig. 4 shows α *vs* T curves at different heating rates for each system. By recording T_α from these curves and applying KAS model, the evolution of apparent E_α throughout the conversion range can be represented. The shape of E_α function in this kind of curves can give valuable insight on the change in reaction steps [33,34].

Fig. 5 shows E_α *vs* α curves obtained from KAS model for the different systems analyzed. In general, changes in apparent E_α are related to the existence of multiple reactions or changes in the limiting stage [33–35]. It is well known that PF cure involves a set of parallel reactions including HMPs formation, condensation as well as different crosslinking chemistries [1,33,36]. Also the presence of water formed during hardening may turn the process even more complicated, contributing to reversible reactions and delaying diffusion control by plasticizing PF network [33,37]. This sometimes leads to a wavy shape of E_α, as reported for PF resole resins by Wang et al. [33], which remarks the complexity of PF cure kinetics. As can be seen in Fig. 5, rather smooth E_α functions were obtained for both modified and unmodified systems. This can be in part attributed to homogeneous crosslinking processes but it also has to be considered that KAS is less sensitive than other methods to changes in E_α [33].

For the reference PF resin the E_α value obtained in this work remains constant (122 kJ/mol) almost throughout the entire process, indicating that it is dominated by a single reaction type [34]. The basic cure mechanism in phenolic resins is based on two main reaction types, namely addition and condensation reactions [1,33,36]. As the former is necessary for cure to proceed, since no hydroxymethyl groups are present in the novolac structure at the end of polymerization, addition mechanism is supposed to be the prevailing one in this case. This also indicates that all the hydroxymethyl groups that are being created react with other aromatic rings, what is favoured in PF by the high proportion of P and thus of activated free ring positions. A similar behaviour in which the curing rate is determined by a single step was observed by Sbirrazzuoli et al. [38] when applying an isoconversional method to non-stoichiometric curing of an epoxy system with a large excess of amine.

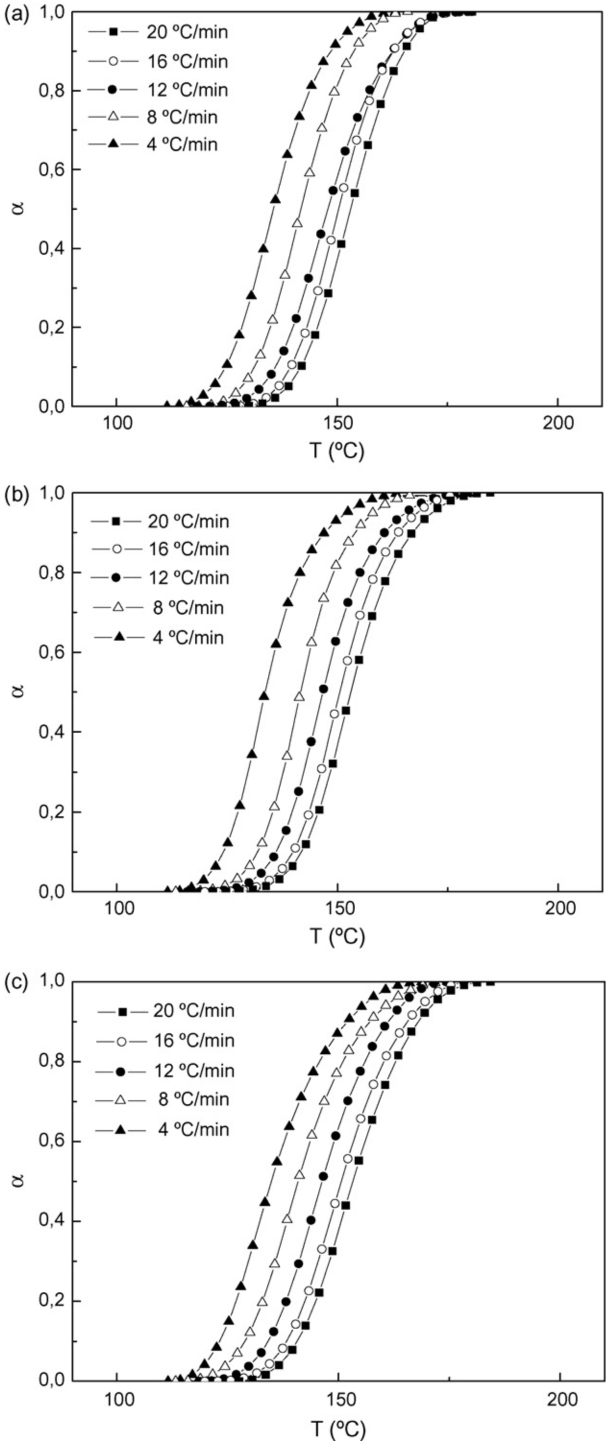

Fig. 4. Evolution of conversion degree with temperature during the curing process of (a) PF, (b) LPF-25 and (c) LPF-45 resins at different heating rates.

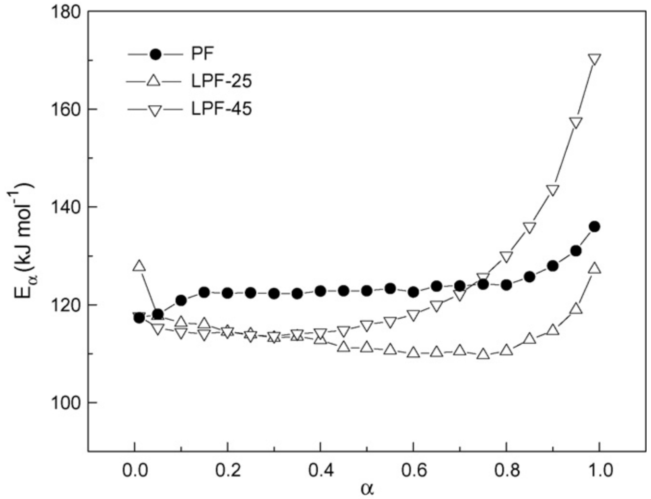

Fig. 5. Evolution of apparent activation energy with conversion degree according to KAS isoconversional model for the curing process of (●) PF, (△) LPF-25 and (▽) LPF-45 resins.

The initial increase shown in the E_α function of PF at the early stages of the cure process fits with that observed by Wang et al. [33] for a high molecular weight PF resole resin and assigned to competitive addition and condensation reactions. On the other hand, the progressive increase at high conversion grade ($\alpha > 0.8$) is related to the simultaneous action of those two mechanisms with contribution of new processes initiated at high temperature [39,40]. Among them, thermal decomposition and rearrangement of methylene ether linkages into methylene bridges, which is known to occur above 170 °C [1,41], are the most likely mechanisms involved.

When 25 wt% P is substituted with L, the E_α function suffers a slight downward dependence until $\alpha = 0.8$. This function shape has been traditionally assigned to a change in the limiting stage from a kinetic to a diffusion regime [34,42], which in LPF-25 resin may be due to the increase in viscosity caused by L introduction; this aspect was reported in a previous work [24]. The same effect was described by Vázquez et al. [43] for curing of tannin-modified PF adhesives. Also the initial quick decrease of E_α in the α region 0–0.5 has been linked to a mechanism of viscosity-related diffusion by different authors [44–46]. However, the general decrease in the apparent activation energy of LPF-25 system is not very pronounced (<7%) in α range 0.05–0.8, suggesting that viscosity has only a moderate effect on the curing process of this resin. The opposite behaviour is found again at $\alpha > 0.8$, where E_α suffered a sharp increase showing the same tendency as reference PF. It is concluded that in LPF-25 the same mechanisms as those commented for PF, as well as new ones promoted by the presence of L, are taking place.

The E_α curve for LPF-45 system remains more or less invariable during the initial steps of the curing process, though a slightly wavy shape is found when it is viewed in detail. In this case the effect of higher viscosity (downward dependence) is thought to be counteracted by competitive condensation reactions (upward dependence) caused by the abundance of L hydroxymethyl groups. Moreover, this latter effect would be the reason for the E_α increment in the α range 0.35–0.65; within these limits, unmodified PF only presents addition reactions and at the same time corresponding temperatures are still too low for decomposition or rearranging reactions, so the competitive mechanism that causes E_α increase can only be related to L reactive groups. The final sharp increase at high conversion values will be again related to the multiple parallel reactions mentioned above, with increased contribution of those originated by L. At this point, it is remarkable to note that the higher the L content in the resin, the higher the final increase in E_α.

Although care should be taken with uncritically accepting these kinetic approximations, because of the high complexity of phenolic resins cure (especially when they are modified with L), they can contribute to clarify the processes involved by simplifying them.

5. Conclusions

Cure kinetics of two lignophenolic resins, having 25 and 45 wt% lignin content, and a commercial novolac have been analyzed by applying several simple and isoconversional kinetic models to empirical data obtained by DSC. According to Ozawa and Kissinger simple models, when phenol is substituted by a sulfonated kraft lignin at a 45 wt% level an important reduction in the activation energy is obtained while there is only small effect at 25 wt% of substitution. This behaviour has been attributed to the incorporation of an extra amount of hydroxymethyl groups in the formulation, as they are present in important quantities in the original lignin structure. KAS isoconversional model shows that addition reactions dominate the curing process in reference PF resin, while the rise in viscosity derived from lignin introduction leads to a moderate change in the limiting stage from a kinetic to a diffusion regime. Condensation reactions, favoured by the abundance of lignin hydroxymethyl groups, acquire high relevance in LPF-45 system cure. Finally, competition with other mechanisms initiated at high temperature is reported at high conversion grades for all cases.

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