



Cure kinetics of lignin–novolac resins studied by isoconversional methods

J.M. Pérez*, M. Oliet, M.V. Alonso, F. Rodríguez

Department of Chemical Engineering, Faculty of Chemical Sciences, University Complutense of Madrid, Avda de la Complutense s/n. 28040 Madrid, Spain

ARTICLE INFO

Article history:

Received 3 December 2008
 Received in revised form 31 December 2008
 Accepted 7 January 2009
 Available online 20 January 2009

Keywords:

Novolac
 Phenolic resins
 Lignosulfonate
 Gelation
 DSC
 TMA

ABSTRACT

The curing process of commercial phenolic, lignin–phenolic and modified lignin–phenolic–novolac resins with hexamethylenetetramine (HMTA) 9 wt% was studied by differential scanning calorimetry (DSC) and thermal mechanical analysis (TMA). Firstly, a demonstration is provided to show that the resin samples studied are associated with an isoconversional principle. Secondly, the isoconversional methods Kissinger–Akahira–Sunose and Friedman are applied to study resin cure using HMTA. These methods yield a dependence of the activation energy on the extent of the cure for three sample resins. Note that either method shows different results in activation energy at low and high conversional degrees. But, both methods have a little variation in activation energy for a curing degree ranging from 10 to 90%.

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1. Introduction

Phenolic resins are widely used in industry because of their flame and chemical resistance, electrical insulation, and dimensional stability [1]. The rise in the cost of petrochemicals derivatives, such as phenol (PF), and its high toxicity have led to the search of natural alternatives for the phenolic resins formulation. Extensive research has been carried out on lignin as an attractive substitute for phenol due to its polyphenolic structure similar to that of phenolic resins [2–5]. There are many works published that focus on lignin–resol resins [6–9], and fewer on the use of lignin–novolac for different applications [5,10].

In the synthesis of thermosets, curing is the most important stage because this reaction sets the final properties of the polymer. It is necessary to study the extent of the curing and kinetic parameters in order to obtain high performance application resins. Differential scanning calorimetry (DSC) is among the techniques employed to study kinetic curing reactions, and is widely applied for measuring an overall extent of the chemical conversion. DSC has the advantage of being based on the same assumption as the heat equation, namely, the proportionality between the rate of heat generation and the rate of the reaction. Curing kinetic parameters of thermosetting polymers can be obtained from isothermal or dynamic data using this thermal analysis technique by applying several different methodologies [11–13]. Novolac resins are very complex systems and their activation energies change depending

on the conversion degree during the curing process. Isoconversional methods reveal changes in the curing kinetics throughout the process and have been applied to the cure of epoxy, epoxy–amine, unsaturated polyester and resol resins using dynamic DSC.

In this paper, the cure kinetics of a lignin–phenolic (LN) and a modified lignin–phenolic–novolac resin were examined by non-isothermal differential scanning calorimetry using a curing agent 9 wt% (hexamethylenetetramine, HMTA). They were set against the cure kinetics of a commercial phenolic resin. Phenol has been substituted partially with ammonium lignosulfonate 30 wt% to obtain the lignin–phenolic–novolac resin. Due to the low reactivity of lignin towards formaldehyde, the other set of resins was synthesized using methylolated softwood ammonium lignosulfonate. In order to demonstrate the isoconversional behavior of these resins, TMA has been used to measure the gel point, in combination with DSC to determine residual heat and gel conversion. Kissinger–Akahira–Sunose and Friedman isoconversional kinetic models have been applied to calculate the activation energy of this phenolic system and to choose, when possible, one of these models to establish the differences between the phenolic resins subject to study.

2. Experimental

2.1. Materials

Commercial novolac resin and hexamethylenetetramine were supplied by Hexion Speciality Chemicals Ibérica, S.A. The softwood ammonium lignosulfonate used was supplied by Borregaard Deutschland as Borresperse AM 320. Lignin–novolac resins were

* Corresponding author. Tel.: +34 91 394 4241; fax: +34 91 394 4243.
 E-mail address: jmperezr@quim.ucm.es (J.M. Pérez).

synthesized using commercial grade phenol, formaldehyde, and oxalic acid.

2.2. Resin preparation

Lignin–novolac (LN) was prepared in laboratory, substituting 30% phenol by liginosulfonate at the beginning of the pre-polymer synthesis. Modified lignin–phenol–formaldehyde–novolac resin was synthesized using methylolated softwood ammonium liginosulfonate 30 wt%. The optimal conditions for methylation and formulation of lignin–novolac and modified lignin–phenolic resins have been reported in previous works [6,14].

2.3. Techniques

A Mettler Toledo TMA 840^e analyzer was employed to measure a sample length expressed as a function of temperature or time. TMA was used to characterize the resin's change from liquid to solid (gelation). The resin was placed between two silica disks (ME-29595), and was tested at different temperatures (413.15, 423.15, 433.15, 443.15 and 453.15 K) to measure the time needed to reach gelation. A periodic force (cycle time = 12 s) of ± 0.05 N was automatically applied to the sample. The TMA gauge was unable to respond to the applied force when the material reached the gelation point. At that stage, the sudden decrease in the amplitude of the oscillations revealed that the sample had reached gelation, and it was eventually cooled ($T = 277.15$ K). A dynamic DSC scan was performed at a heating rate of 10 K/min to determine the residual heat and the gel conversion.

DSC runs were carried out using a Mettler-Toledo DSC 821e and pressure medium pans. The mixtures of resins and curing agents were cured in 120 μ L crucibles, at heating rates of 2, 4, 6, 8, 10, 12, 14, 16 and 20 K/min with temperature ranging from 303 to 523 K. The obtained data were applied to the Kissinger–Akahira–Sunose and Friedman methods.

2.4. Kinetic methods

The isoconversional methods employed in this work are based on dynamic DSC analysis. The equation for the reaction rate employed to study the curing kinetics of the resins can be expressed, in general, as:

$$\frac{d\alpha}{dt} = k \cdot f(\alpha) \quad (1)$$

considering that the rate Eq. (1) is valid for dynamic curing and that $d\alpha/dt = \beta(d\alpha/dT)$, where β is the heating rate (K/min) and k is the rate constant expressed by the temperature-dependent Arrhenius equation, Eq. (1) can be written as:

$$\beta \frac{d\alpha}{dT} = A \cdot e^{(-E_a/RT)} \cdot f(\alpha) \quad (2)$$

where T is the temperature, A is the pre-exponential factor, E is the activation energy, which is independent of the conversion, R is the gas constant and α is the extent of the cure.

The Kissinger–Akahira–Sunose's model-free method [15] that can be originally obtained through the derivative of Eq. (2) is as follows:

$$\ln \left(\frac{\beta}{T^2} \right) = \ln \left(\frac{R \cdot A}{E_a \cdot g(\alpha)} \right) - \frac{E_a}{R} \cdot \frac{1}{T} \quad (3)$$

in this case, the method does not require the knowledge of the conversion-dependent function ($f(\alpha)$ or $g(\alpha)$), and it only assumes that the process follows the same mechanism of reaction for a given conversion degree, regardless of the curing temperature.

Friedman's isoconversional method [16] relates the logarithm of the reaction rate to the inverse temperature for a given curing degree. Thus, from the expression of Eq. (2), every heating rate can be written as:

$$\ln \left[\beta_i \left(\frac{d\alpha}{dT} \right)_{\alpha,i} \right] = \ln[f(\alpha_i)A_\alpha] - \frac{E_\alpha}{R \cdot R_{\alpha,i}} \quad (4)$$

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

3. Results and discussion

3.1. Isoconversional principle

The extent of cure at the gel point (α_{gel}) concerning different temperatures for phenolic (PF), lignin–phenolic (LN) and modified lignin–phenolic (MLN) novolac resins was studied by TMA and DSC. The TMA runs allowed the material to reach gelation, while the DSC measured the residual heat and the degree of gel conversion. More detailed information on this has been published [11].

The values obtained for α_{gel} are 51.3, 30.3 and 30.2% for the PF, LN and MLN resins with HMTA 9 wt%, respectively. Note that for all samples studied, gelation follows the isoconversional principle because α_{gel} values are independent of the curing temperature employed.

Gelation observed for LN and MLN resins with HMTA 9 wt% is remarkably reduced compared to that for commercial resin (PF). This means that gelation and therefore curing take place probably much faster in the LN and MLN resins. There are two phenomena that may explain this: lignin has less free sites in the aromatic ring compared to phenol, but, lignin also presents additional methylol groups in its structure, and even modified lignin introduces extra functional groups in the aromatic ring that facilitate the curing reaction [13]. The former phenomenon would explain what happens with lignin resins. At the same time, their enthalpy is lower than that of PF resin (61.5, 80.2 and 137.0 J/g of LN, MLN and PF resins, respectively). The latter can explain what happens when comparing enthalpy of two lignin–novolac resins. A higher value of enthalpy in MLN means more functional groups than LN resin to crosslink.

3.2. Curing kinetics

The curves of curing degree against temperature (10 K/min) for the phenol–formaldehyde, lignin–phenolic and modified lignin–phenolic–novolac resins with HMTA 9 wt% are shown in Fig. 1. LN and MLN need less temperature to begin the cure reaction compared to PF resin. The data figures and those obtained for the rest of heating rate assayed [17] were applied to isoconversional methods Kissinger–Akahira–Sunose (KAS) and Friedman to calculate the kinetic parameters of the curing process for novolac samples.

Activation energy, correlation coefficient (R^2) and standard deviation values (Table 1) can be obtained (Fig. 2) by the KAS method (Eq. (3)). Thus, the average values of the activation energy of PF, LN and MLN resins with curing agent 9 wt% are 117.8 ± 10.3 , 92.5 ± 3.1 and 89.8 ± 3.9 kJ/mol, respectively. They remain constant almost throughout the process, indicating that it is dominated by a single reaction type [18].

In most cases, correlation coefficients (R^2) vary between 0.98 and 0.99. The activation energy values of the PF resin with HMTA 9 wt% begin to decrease slightly, then tend to be constant ($\alpha = 20\%$), while LN and MLN resins with HMTA 9 wt% do not show changes in the activation energy. The LN and MLN resins present similar values; however, these results are different compared to novolac

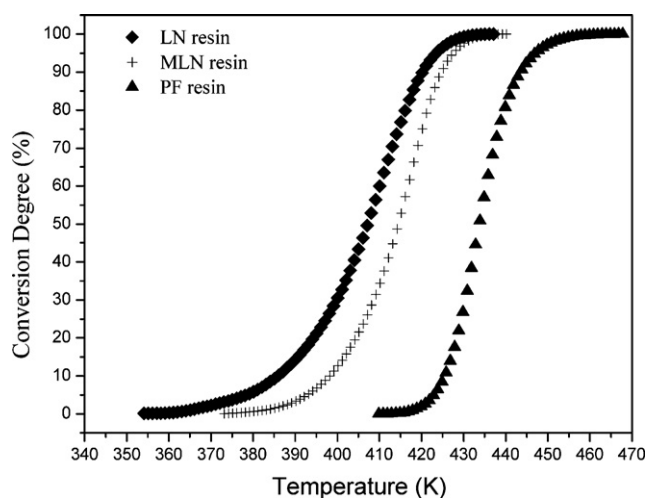


Fig. 1. Curing degrees at 10K/min of phenolic, lignin-phenolic and modified lignin-phenolic resins vs. temperature.

Table 1

Curing kinetic correlation coefficient and standard deviation obtained by KAS isoconversional method.

α	PF		LN		MLN	
	R	SD	R	SD	R	SD
2	0.987	0.119	0.924	0.285	0.895	0.347
10	0.994	0.084	0.977	0.157	0.976	0.160
20	0.995	0.077	0.988	0.114	0.987	0.119
30	0.995	0.075	0.992	0.091	0.991	0.099
40	0.995	0.075	0.995	0.077	0.993	0.085
50	0.995	0.076	0.996	0.069	0.994	0.077
60	0.994	0.078	0.996	0.068	0.995	0.072
70	0.994	0.084	0.996	0.069	0.995	0.070
80	0.992	0.096	0.995	0.073	0.995	0.072
90	0.986	0.121	0.994	0.081	0.994	0.077
95	0.981	0.143	0.992	0.090	0.994	0.080
100	0.969	0.181	0.997	0.055	0.992	0.090

R: correlation coefficient. SD: standard deviation.

commercial resin. This fact could be attributed to a different reaction mechanism during the curing process, given the ortho and/or para vacant sites in the aromatic ring of phenol and/or lignin [13]. Thus, the reaction of phenol with HMTA is a complex system to study because the molecule has three reactive sites. Looney et al. [19] observed that the majority of the HMTA in solid state ^{13}C Nuclear Magnetic Resonance (NMR) runs is consumed in the free ortho positions of phenol, thus forming benzoxazine as intermediate, while in the free para positions it leads to benzylamines that decompose to methylene-bridged aromatic residues. However,

Table 2

Curing kinetic correlation coefficient and standard deviation obtained by Friedman's isoconversional method.

α	PF			LN			MLN		
	$\ln A$	R	SD	$\ln A$	R	SD	$\ln A$	R	SD
2	10.704	0.904	0.279	12.238	0.954	0.178	7.478	0.901	0.522
10	18.180	0.949	0.198	15.212	0.985	0.121	13.764	0.918	0.333
20	20.379	0.963	0.183	17.029	0.990	0.107	15.128	0.943	0.223
30	20.189	0.965	0.183	18.349	0.992	0.095	15.686	0.969	0.165
40	21.536	0.964	0.190	19.091	0.993	0.097	16.033	0.984	0.121
50	21.714	0.961	0.203	18.813	0.991	0.101	16.225	0.987	0.106
60	21.650	0.956	0.218	17.609	0.988	0.115	16.245	0.991	0.092
70	21.704	0.946	0.247	16.445	0.987	0.115	16.104	0.992	0.085
80	21.310	0.932	0.282	15.559	0.985	0.121	15.715	0.992	0.083
90	21.527	0.912	0.358	14.583	0.978	0.150	14.855	0.991	0.087
95	20.614	0.899	0.425	14.274	0.971	0.174	14.198	0.990	0.093
100	2.073	0.887	0.615	–	–	–	11.432	0.977	0.141

$\ln A = E/RT - f(\alpha_i)$. R: correlation coefficient. SD: standard deviation.

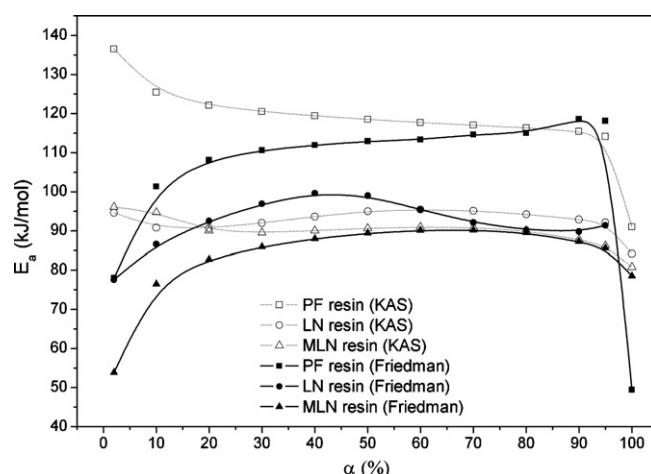


Fig. 2. Activation energy of resin curing determined by the KAS and Friedman's isoconversional methods.

lignin has less free sites for reacting with the curing agent, but this circumstance is balanced because lignin presents more methylol groups to build a network.

Friedman's isoconversional method is different from the other because, in this case, reaction rates ($r = d\alpha/dt$) at different curing degrees are obtained from the thermograms determined by dynamic DSC runs for a given temperature. However, the other method correlates directly the curing degrees with the inverse temperature, reducing error in the calculated kinetic parameters.

The results of the activation energy, the logarithm of the pre-exponential factor (A), correlation coefficient (R^2) and standard deviation (SD) for three resins by Friedman's method are shown in Table 2. The average value of activation energy and standard deviation for PF, LN and MLN resins is 112.4 ± 5.0 , 93.4 ± 4.2 and 86.5 ± 4.2 kJ/mol, respectively (activation energies corresponding to 2 and 100% were not considered). The results obtained when calculating activation energy averages by Friedman's method are very close to those given by KAS method. The tendency of this kinetic parameter is different with respect to KAS method, due to the error associated with the determination of reaction rate by Friedman's method (Eq. (4)). In Fig. 2 (Friedman's results), PF and MLN resins with HMTA 9 wt% show initially an increase in the activation energy (up to $\alpha = 20\%$). It tends later to increase slightly ($\alpha > 20\%$). In the case of MLN resin, the activation energy decreases when the curing degree is over 80%. This can be explained as a result of the transition in kinetics from chemical reaction to diffusion control [11,20]. Activation energy in LN resin increases from 75 up to 100 kJ/mol for $\alpha = 0$ –40%. The E_a values decrease later due to an increase in

the molecular weight of the resin and diffusion-controlled kinetics [21]. This method does not detect the changes in activation energy that the other methods revealed. Possibly, the deviation of these data is the result of calculating reaction rate by Friedman's method.

In short, the results obtained using Friedman's and KAS methods reveal important differences due to systematic error in activation energy calculation [22]. For instance, the activation energy values are always lower in Friedman's method. In addition, this method shows different tendency regarding activation energy compared to the other methods. On the one hand, an advantage of Friedman's method is the determination of the pre-exponential factor, although a $g(\alpha)$ function is needed.

4. Conclusions

It is possible to establish that the cure of commercial, lignin–phenolic and modified lignin–phenolic–novolac resins with HMTA 9 wt% agrees with the isoconversional principle. This behavior has been experimentally verified by TMA. The conversion degree (α_{gel}) is determined through post-curing by DSC the resin that was gelled by TMA.

The isoconversional methods can be applied to study the curing process of these polymers. Thus, the experimental results show the dependence of activation energy on the curing degree of commercial, lignin–phenolic and modified lignin–phenolic resins. Averages of activation energies show that both models are suitable to study lignin–phenolic resins curing process. At this point, Friedman's method presents higher error in low and high conversion degrees (2–100%). In addition, the variation of the activation energy at different curing degrees shows little variation of activation energy in 10–90% conversion degree range. In spite of the similarity of the results, the LN and MLN with HMTA 9 wt% resins show inferior activation energies compared to commercial novolac resin.

Acknowledgement

The authors are grateful to the Ministerio de Ciencia y Tecnología (Ministry of Science and Technology of Spain) for its financial support (project CTQ2007-64071).

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