

Curing kinetics of lignin-novolac phenolic resins using non-isothermal methods

J. M. Pérez · F. Rodríguez · M. V. Alonso · M. Oliet · J. C. Domínguez

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Abstract The curing kinetics of lignin-novolac and methylolated lignin-novolac resins were studied using non-isothermal methods employing differential scanning calorimetry (DSC) at different heating rates. The Belichmeier, Ozawa and Kissinger methods were applied, which give the kinetic parameters of the curing process studied. In addition, the model-fitting Coats-Redfern method was used to analyze the experimental data. The kinetic study evaluated the effect of the lignin (softwood ammonium lignosulfonate), methylolated or not, on the resin curing process. Results for lignin-novolac and modified lignin-novolac resins were compared with a commercial novolac resin as a reference. When lignosulfonate is modified by methylolation and is incorporated in the novolac resin, there is an important reduction in activation energy. The lignin-novolac showed slightly higher values of activation energy than methylolated-lignin resins, but lower values than commercial resins. This behavior has been attributed to the extra methylol groups introduced by lignosulfonate.

Keywords Curing kinetics · Differential scanning calorimetry · Lignosulfonate · Phenolic resins

Introduction

In recent years, due to the increase of phenol cost, researchers have studied the partial substitution of

compounds with similar structures into phenolic resins [1–3]. One of these possible substitutes is lignin, a complex polyphenolic natural polymer, which can be obtained using different pulping processes. Only lignosulfonates extracted from the sulphite process are available in great quantities. Among them, ammonium lignosulfonates have been reported to be the most adequate to substitute phenol because the final properties of phenolic resins are better using this type of lignosulfonate rather than calcium or sodium lignosulfonates [3, 4]. However, this natural polymer has to be modified to increase its reactivity towards formaldehyde [4, 5].

Novolac resins synthesized with curing agents are thermosetting polymers widely used in molding compounds, refractories, and textile felts. The present work is focused on the evaluation of the curing kinetic parameters of novolac, lignin-novolac and modified lignin-novolac resins that could be used as textile felts in the manufacture of automobile structures. These phenolic resin-bonded textile felts may be considered to be a fiber-reinforced plastic. In addition, these fibers are comprised of textile scraps recycled from the textile industry [6].

The curing step of phenolic thermosetting polymers has great influence on the final properties of the material. Therefore, it is necessary to study the curing kinetics of these polymers, which are not well-known in the case of phenolic novolac resins. Among different techniques employed to study the curing kinetics of these resins, differential scanning calorimetry (DSC) is frequently used because it not only reveals the temperature-dependent behavior of a material for a given chemical process, but it also measures the heat associated with the curing process as a function of temperature. DSC technique has the advantage of being based on the relationship between the heat flow and the reaction rate of the resin curing process [7–9]. Thus, it is

J. M. Pérez · F. Rodríguez · M. V. Alonso · M. Oliet (✉) · J. C. Domínguez
Departamento de Ingeniería Química, Facultad de Ciencias Químicas, Universidad Complutense, Avda de la Complutense, s/n, 28040 Madrid, Spain
e-mail: moliet@quim.ucm.es

possible to calculate the total and partial heats, the cure degree of resins and the reaction rate of the process.

In this work, four non-isothermal methods were used to determine the kinetic parameters from the curing processes of lignin-novolac (LN), methylolated lignin-novolac (MLN) and commercial novolac (PF) resins using DSC. The results obtained for the cure of LN and MLN resins were compared with those attained for PF resins. This comparison allows for evaluation of the suitability of partial substitutions of phenol in novolac resins using softwood ammonium lignosulfonate.

The models of Belichmeier, Ozawa, Kissinger, and Coats-Redfern's were applied to obtain kinetic parameters of novolac curing from dynamic DSC scans [10–13]. Belichmeier's method is an empirical model, characterized by simplicity because a single scan allows all kinetic parameters to be determined. Ozawa and Kissinger's methods are based on the variation of the exotherm peak temperature with heating rate, and Coats-Redfern's model employs a conversion function to calculate the kinetic parameters. Dynamic methods were used instead of isothermal methods because isothermal runs cannot be carried out at high temperatures when the reaction rate of curing phenolic resins is too fast and significant decomposition may occur during the first step of the process [14].

The present work is original because while there are some kinetic studies on curing phenolic resin resins [9, 15–22] and novolac-type substitution with a sulfonated Kraft lignin [23], but there are no curing kinetics studies on novolac resins with lignosulfonates.

Experimental

Materials

A commercial phenol-formaldehyde novolac resin (water content <0.4 wt%, free phenol <0.2%, flow distance of 25–40 mm) and hexamethylenetetramine (9 wt% curing agent in relation to resin content) were supplied by Hexion Speciality Chemicals Ibérica, S.A. The softwood ammonium lignosulfonate was supplied by Borregaard Deutschland as Borresperse AM 320. Lignin-novolac and modified lignin-novolac resins were synthesized using commercial grades of phenol, formaldehyde, and oxalic acid.

Preparation of LN and MLN resins

A commercial novolac resin was tested as a reference. This product was obtained by the polymerization of formaldehyde and phenol in an acidic medium. Lignin-novolac was formulated in the laboratory by substituting phenol with lignosulfonate at the beginning of the pre-polymer

synthesis. Methylolated lignin-novolac resin was synthesized under the same operating conditions as LN resin using lignosulfonate modified by methylation [4]. The formulation details of the LN and MLN resins were reported in a previous work [24]. The substitution of phenol by ammonium lignosulfonate was fixed at 30 wt% in both samples because higher proportions do not produce suitable resins [16, 25]. The three resins tested were cured with 9 wt% hexamethylenetetramine (HMTA).

Differential scanning calorimetry measurements

DSC runs were performed using a Mettler-Toledo DSC821^e with pressure medium pans of 120 μ L volume. Resin samples and the curing agent were mixed in a mill and cured by dynamic DSC. Belichmeier and Coats-Redfern methods require only one experiment. Thus, a heating rate of 10 K min⁻¹ was chosen as a reference because this is the most common value used to determine kinetic parameters of resin curing with a single heating rate [7, 8, 26–28]. Although Ozawa and Kissinger's methods only need three tests at different heating rates, in this work nine heating rates were utilized (2, 4, 6, 8, 10, 12, 14, 16, and 20 K min⁻¹) scanning the temperature range from 303 to 523 K.

Kinetic methods

Belichmeier's method is based on a simple scan by DSC to determine activation energy [10]. Other dynamic methods, such as Ozawa and Kissinger's models [11, 12], are more accurate in determining the kinetic curing parameters of resins using multiple heating rates. These methods are based on the relationship between the reciprocal absolute peak temperature and the heating rate [29, 30]. Coats-Redfern's method employs several conversion functions to calculate the kinetic parameters of resin curing [13].

Belichmeier's model is based on the fact that resin curing degree versus time curves are almost independent of reaction order for small values of conversion. This curve is expressed by Eq. 1:

$$E_a \approx \frac{R \cdot T}{\alpha} \cdot \frac{1}{\beta} \frac{d\alpha}{dt} = \frac{R \cdot T^2}{\alpha} \cdot \frac{d\alpha}{dT} \quad (1)$$

where T is the temperature in K at which the reaction rate is 40% of its maximum value, $d\alpha/dt$ is the rate of conversion at temperature T , β is the heating rate (K min⁻¹), α is the degree of resin conversion up to temperature T , and R is the universal gas constant (8.31 J K⁻¹ mol⁻¹). To evaluate the activation energy of the kinetic process, it is necessary to know three parameters: temperature, $d\alpha/dT$ values, and α .

Ozawa's method establishes a simple relationship between the activation energy E_a and the heating rate β as

a function of peak temperature T_p . This T_p value is the temperature at which the DSC thermogram exhibits maximum enthalpy. Ozawa’s method allows determination of the activation energy E_a and the pre-exponential factor using the following expression:

$$\log \beta = A - 0.4567 \cdot \frac{E_a}{R \cdot T_p} \tag{2}$$

where,

$$A = \log \frac{k_0 \cdot E_a}{g(\alpha) \cdot R} \tag{3}$$

and the function $g(\alpha)$ is defined as:

$$g(\alpha) = \int_{\alpha_0}^{\alpha_p} \frac{1}{f(\alpha)} d\alpha \tag{4}$$

where α is the degree of conversion, α_0 represents the initial conversion degree of resin, α_p is the conversion degree at peak temperature, and $f(\alpha)$ is a function of conversion. Thus, activation energy can be obtained from the slope of $\log \beta$ versus $1/T_p$. However, this method does not give information about the kinetics reaction order for resin curing.

Kissinger’s method is taken as the rate equation that relates the rate of resin conversion at a constant temperature dx/dt with a function of the concentration of reagents $f(\alpha)$ through a rate constant $k(T)$. The equation can be expressed as follows:

$$r = \frac{dx}{dt} = k(T) \cdot f(\alpha) \tag{5}$$

where r is the reaction rate and $f(\alpha)$ is a conversion function, which depends on the kinetic model applied.

Substituting $k(T)$ by Arrhenius’ equation in Eq. 5:

$$\frac{dx}{dt} = k_0 \cdot e^{(E_a/R \cdot T)} \cdot f(\alpha) \tag{6}$$

The evolution of the conversion degree of resin at any time can be found as the product of its variation with respect to temperature and the heating rate β , which can be expressed as:

$$\frac{dx}{dt} = \frac{dx}{dT} \cdot \frac{dT}{dt} = \frac{dx}{dT} \cdot \beta \tag{7}$$

Equations 6 and 7 may be combined as follows:

$$\frac{dx}{dt} = \beta \cdot \left(\frac{dx}{dT} \right) = f(\alpha) \cdot k_0 \cdot e^{E_a/R \cdot T} \tag{8}$$

Rearranging Eq. 8 and integrating from $T_0 = \alpha_0$ and $T_p = \alpha_p$,

$$\int_{\alpha_0}^{\alpha_p} \frac{dx}{f(\alpha)} = \frac{k_0}{\beta} \int_{T_0}^{T_p} e^{E_a/R \cdot T} \cdot dT \approx \frac{k_0 \cdot E_a}{\beta \cdot R} \cdot p(\alpha) \tag{9}$$

where $p(x)$ is the named p -function defined by Doyle [31], which can be re-written as:

$$\int_{x_T}^{\infty} \frac{\exp(-x)}{x^2} dx = p(x) \tag{10}$$

Depending on the approximation, this p -function can be obtained by different methods. An approximation of the p -function was proposed by Murray-White [32]:

Table 1 Expressions for $f(\alpha)$ and $g(\alpha)$ functions used in Coats-Redfern’s method [29]

| Mechanism | Symbol | $f(\alpha)$ | $g(\alpha) = \int_0^{\alpha} \frac{1}{f(\alpha)} d\alpha$ |
|---|--------|---|---|
| Two-dimensional nucleation (Avrami 1 equation) | A_2 | $2 \cdot (1 - \alpha) \cdot [-\text{Ln}(1 - \alpha)]^{1/2}$ | $[-\text{Ln}(1 - \alpha)]^{1/2}$ |
| Two-dimensional growth of nuclei (Avrami 2 equation) | A_3 | $3 \cdot (1 - \alpha) \cdot [-\text{Ln}(1 - \alpha)]^{2/3}$ | $[-\text{Ln}(1 - \alpha)]^{1/3}$ |
| Three-dimensional growth of nuclei (Avrami 3 equation) | A_4 | $4 \cdot (1 - \alpha) \cdot [-\text{Ln}(1 - \alpha)]^{1/4}$ | $[-\text{Ln}(1 - \alpha)]^{1/4}$ |
| Zero-order mechanism | R_1 | 1 | α |
| Phase-boundary-controlled reaction (contracting cylinder) | R_2 | $(1 - \alpha)^{1/2}$ | $[1 - (1 - \alpha)^{1/2}]$ |
| Phase-boundary-controlled reaction (contracting sphere) | R_3 | $(1 - \alpha)^{2/3}$ | $[1 - (1 - \alpha)^{1/3}]$ |
| One-dimensional diffusion | D_1 | $1/2\alpha$ | α^2 |
| Two-dimensional diffusion | D_2 | $1/[-\text{Ln}(1 - \alpha)]$ | $(1 - \alpha) \cdot \text{Ln}(1 - \alpha) + \alpha$ |
| Three-dimensional diffusion (Jander equation) | D_3 | $\frac{3 \cdot (1 - \alpha)^{2/3}}{2 \cdot [1 - (1 - \alpha)^{1/3}]}$ | $[1 - (1 - \alpha)^{1/3}]^2$ |
| Three-dimensional diffusion (Ginsting-Brounshtein equation) | D_4 | $\frac{3}{2 \cdot [(1 - \alpha)^{1/3} - 1]}$ | $(1 - \frac{2}{3}\alpha) - (1 - \alpha)^{2/3}$ |
| First order reaction | F_1 | $(1 - \alpha)$ | $-\text{Ln}(1 - \alpha)$ |
| Second order reaction | F_2 | $(1 - \alpha)^2$ | $\frac{1}{(1 - \alpha)}$ |
| Third order reaction | F_3 | $(1 - \alpha)^3$ | $\frac{1}{(1 - \alpha)^2}$ |

$$p(x) = \frac{e^{-x}}{x^2} \quad (11)$$

Substituting Eq. 11 into 9 and with $g(x)$ fitted to the following expression, $n(1-p)n-1 \approx 1$, Kissinger's method can be expressed as follows:

$$-\ln\left(\frac{\beta}{T_p^2}\right) = \frac{Ea}{R \cdot T_p} - \ln\left(\frac{k_0 \cdot R}{Ea}\right) \quad (12)$$

Kissinger suggested a similar method to Ozawa, which relates $-\ln(\beta/T_p^2)$ to the inverse of the peak temperature. The representation of Eq. 12 allows calculating both activation energy and pre-exponential factors for the curing process of novolac resins.

When the p -function is substituted by the Coats-Redfern's approximation [13]:

$$p(x) = \frac{e^{-x}}{x^2} \cdot \left(1 - \frac{2}{x}\right) \quad (13)$$

and it is supposed that $\ln(1 - 2R/Ea)$ tends to zero, then the following expression describes Coats-Redfern's method:

$$\ln\left(\frac{g(x)}{T^2}\right) = \ln\left(\frac{k_0 \cdot R}{\beta \cdot Ea}\right) - \frac{Ea}{R \cdot T} \quad (14)$$

where $g(x)$ is a function that depends on the kinetic model applied (Table 1). The Coats and Redfern method is one of the most popular model-fitting methods. This method uses the asymptotic series expansion for approximating the exponential integral $p(x)$ to obtain Eq. 14. The representation of $\ln(g(x)/T^2)$ vs. $1/T$ with the substitution of a $g(x)$ function allows the activation energy and the pre-exponential factor of resin curing kinetics to be obtained from the slope of the line and the origin ordinate, respectively.

Results and discussion

Thermograms normalized by the resin baseline cured at different heating rates are shown in Fig. 1. In each of the thermograms of the three samples studied, one peak (T_p) represents the condensation reaction between the phenol (PF resin), the phenol/lignin (LN resin) or the phenol/modified-lignin (MLN resin) and the formaldehyde.

Resol resins produce two peaks, which is unlike novolac resins [9, 17]. The first of these peaks appears at lower temperatures and it is the result of the free formaldehyde in the resol resin, which can lead to a different product. The second peak is due to condensation reactions between the phenol and the formaldehyde, or the methylolated ligno-sulfonate in the case of lignin-resol phenolic resin [33]. Note that the lignin-novolac, modified lignin-novolac and novolac resins do not show the first peak of the resol resins

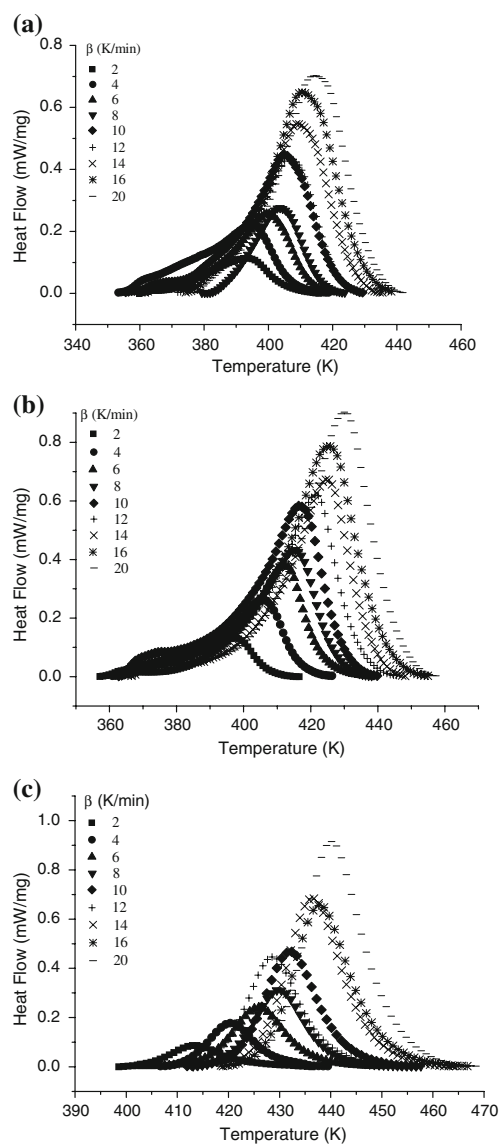


Fig. 1 DSC thermograms of lignin-novolac, modified lignin-novolac and novolac resins curing: **a** LN, **b** MLN, **c** PF

because the addition reactions take place during synthesis. The peak temperatures of LN and MLN resins are lower than that of commercial resin (Fig. 1) and they can be a consequence of peak broadening, but this does not necessarily imply that the curing process of LN and MLN resins can be faster than that of the commercial PF resins [9, 33].

In order to obtain the kinetic parameters of the resin curing process, the data plotted in Fig. 1 have been treated by the methods described above. It is necessary to determine reaction rate, total heat, partial heats and the resin cure degree (α). The peak temperatures and reaction heats of the curing process for LN, MLN and PF resins at the nine heating rates employed are shown in Table 2. The enthalpies of all cured resins remain nearly constant and do

Table 2 Peaks temperatures and reaction heats of novolac curing process at different heating rates

| β (K min ⁻¹) | LN | | MLN | | PF | |
|-----------------------------------|--------------|------------------------------------|--------------|------------------------------------|--------------|------------------------------------|
| | T_p (K) | ΔH (J g ⁻¹) | T_p (K) | ΔH (J g ⁻¹) | T_p (K) | ΔH (J g ⁻¹) |
| 2 | 392.4 | 69.08 | 397.4 | 87.19 | 413.1 | 131.16 |
| 4 | 398.8 | 55.89 | 406.1 | 86.70 | 420.8 | 129.49 |
| 6 | 404.4 | 55.26 | 411.8 | 72.67 | 426.0 | 135.40 |
| 8 | 407.7 | 65.55 | 415.0 | 78.38 | 428.8 | 134.64 |
| 10 | 410.4 | 50.39 | 418.1 | 69.42 | 432.2 | 140.47 |
| 12 | 411.6 | 61.25 | 420.4 | 74.11 | 434.1 | 144.36 |
| 14 | 416.2 | 63.59 | 423.6 | 78.24 | 437.2 | 141.47 |
| 16 | 418.9 | 69.05 | 426.1 | 84.77 | 438.7 | 136.04 |
| 20 | 422.3 | 63.43 | 429.8 | 90.43 | 441.0 | 140.37 |

not decrease with heating rate as was observed in a previous study on resol resins [9]. However, the commercial cured resins show higher reaction heats than that of LN and MLN cured resins. The lignosulfonate incorporated in the formulation of the novolacs contains fewer free ring positions than phenol and more steric impediments, but it also introduces extra methylol groups similar to those produced by formaldehyde during resins curing, what will act in the opposite way [34]. According to the results of the enthalpy calculations, MLN and LN resins exhibit similar behaviors. PF enthalpies are higher than those of the MLN and LN resins.

The peak temperatures of the LN and MLN resins are also less than that of the commercial resin (Fig. 1; Table 2) and, as has been noted above, the results can be a consequence of peak broadening and not faster curing for lignin resins [33].

Belichmeier's method allows for the determination of the activation energy of resin curing kinetics using Eq. 1 if one knows the temperature (T) at which the reaction rate is 40% of the maximum process rate. The curing activation energy values of lignin-novolac, modified lignin-novolac and commercial novolac resins are shown in Table 3.

Lignin-novolac and modified lignin-novolac resins present similar activation energy values. Thus, the modification of lignosulfonate to increase its reactivity towards

formaldehyde for the formulation of MLN resin does not remarkably affect the novolac curing. In addition, the activation energy values obtained using Belichmeier's method are lower in lignin-novolac and methylolated lignin-novolac than in the commercial resin. This agrees with the effect mentioned before: lignosulfonate incorporated in novolacs introduces extra methylol groups. The positive effect of lignosulfonates during curing of phenolic resins has been probed by Matuana [35], who found that lignosulfonates improve novolac curing reactions through a decrease in the activation energy of the process.

Despite the simplicity of Belichmeier's method, the data obtained are influenced by noise and baseline corrections. However, this method gives an order of magnitude of the activation energy of resin curing. While Belichmeier's method employs a single run, Ozawa and Kissinger's methods simultaneously utilize several heating rates. The results obtained from the linear fit of kinetic data of applied models for novolac, lignin-novolac and methylolated lignin-novolac resin curing are shown in Table 3. In the Ozawa's method, the A parameter, related to the origin ordinate, changes with the activation energy value, but keeps the same order of magnitude. Experimental data on resin curing satisfactorily fit to assayed methods, as is shown by its R^2 value. The activation energy values obtained using the Ozawa and Kissinger methods are lower for lignin-novolac and methylolated lignin-novolac than that of commercial resin. This can be explained by the fact that lignin-novolac and modified lignin-novolac resins have more functional groups and NH_4^+ from ammonium lignosulfonate, which enhance crosslinking reactions in relation to commercial resins. Similar to the findings of Matuana [35], evidence of the positive effect of lignosulfonates during curing of phenolic resins was observed in the present study. LN and MLN resins cured exhibit, in both methods, similar activation energies (about 100 kJ mol⁻¹). These data are in agreement with the E_a values determined by Tejado [23], who applied the Ozawa and Kissinger models to the curing of novolac formulated with sulfonated Kraft lignin.

According to the activation energy values for the curing of lignin-novolac and modified lignin-novolac resins, these polymers are suitable to replace commercial resin in

Table 3 Activation energies of curing kinetics of lignin-novolac, modified lignin-novolac and commercial resins according to Ozawa, Kissinger and Belichmeier's methods

| Resin | Ozawa | | | Kissinger | | Belichmeier |
|-------|-------|--|-------|--|-------|--|
| | A^a | E_a (kJ mol ⁻¹) \pm standard error | R^2 | E_a (kJ mol ⁻¹) \pm standard error | R^2 | E_a (kJ mol ⁻¹) \pm standard error |
| LN | 14.8 | 103.6 \pm 3.7 | 0.986 | 101.4 \pm 3.2 | 0.976 | 102.9 \pm 8.6 |
| MLN | 13.7 | 96.9 \pm 1.9 | 0.998 | 94.6 \pm 1.9 | 0.990 | 96.8 \pm 9.8 |
| PF | 15.9 | 116.9 \pm 2.1 | 0.998 | 114.6 \pm 2.6 | 0.988 | 135.2 \pm 9.9 |

^a $A = \log \frac{k_0 \cdot E_a}{g(x) \cdot R}$

Table 4 Kinetic parameters of curing kinetics of lignin-novolac, modified lignin-novolac and commercial resins according to Coats-Redfern's method

| $g(\alpha)$ | Parameter | Resin | | |
|----------------|-----------|---------|---------|----------|
| | | LN | MLN | PF |
| A ₂ | Ea | 91.8 | 58.9 | 133.6 |
| | k_0 | 2.2E+11 | 1.1E+7 | 6.9E+15 |
| | R^2 | 0.962 | 0.919 | 0.876 |
| A ₃ | Ea | 58.9 | 37.0 | 96.7 |
| | k_0 | 1.1E+7 | 1.2E+5 | 1.0E+10 |
| | R^2 | 0.960 | 0.910 | 0.906 |
| A ₄ | Ea | 42.5 | 26.1 | 63.2 |
| | k_0 | 6.5E+4 | 3.6E+2 | 1.3E+7 |
| | R^2 | 0.956 | 0.898 | 0.863 |
| R ₁ | Ea | 125.3 | 85.5 | 168.1 |
| | k_0 | 2.0E+15 | 1.6E+10 | 4.3E+19 |
| | R^2 | 0.819 | 0.799 | 0.659 |
| R ₂ | Ea | 147.5 | 99.6 | 202.0 |
| | k_0 | 1.1E+18 | 7.9E+11 | 4.0E+23 |
| | R^2 | 0.885 | 0.927 | 0.746 |
| R ₃ | Ea | 158.4 | 106.2 | 219.2 |
| | k_0 | 2.0E+19 | 4.4E+12 | 3.8E+25 |
| | R^2 | 0.913 | 0.889 | 0.786 |
| D ₁ | Ea | 257.3 | 177.7 | 343.5 |
| | k_0 | 7.1E+31 | 6.6E+21 | 2.67E+40 |
| | R^2 | 0.826 | 0.812 | 0.669 |
| D ₂ | Ea | 287.6 | 195.6 | 392.5 |
| | k_0 | 4.0E+35 | 9.6E+23 | 1.6E+46 |
| | R^2 | 0.866 | 0.848 | 0.721 |
| D ₃ | Ea | 323.5 | 219.2 | 445.7 |
| | k_0 | 5.6E+39 | 3.8E+26 | 1.6E+52 |
| | R^2 | 0.918 | 0.895 | 0.792 |
| D ₄ | Ea | 293.8 | 201.0 | 398.5 |
| | k_0 | 6.2E+35 | 1.2E+24 | 2.1E+46 |
| | R^2 | 0.879 | 0.863 | 0.736 |
| F ₁ | Ea | 190.3 | 124.5 | 274.5 |
| | k_0 | 1.2E+24 | 4.5E+15 | 1.0E+33 |
| | R^2 | 0.964 | 0.865 | 0.881 |
| F ₂ | Ea | 209.4 | 119.3 | 358.4 |
| | k_0 | 5.1E+27 | 1.2E+16 | 2.2E+44 |
| | R^2 | 0.649 | 0.552 | 0.796 |
| F ₃ | Ea | 425.6 | 245.2 | 724.1 |
| | k_0 | 2.7E+56 | 2.4E+33 | 3.1E+89 |
| | R^2 | 0.656 | 0.565 | 0.799 |

Ea: [kJ mol⁻¹], k_0 : [min⁻¹]

textile-felts applications. The results presented here show that LN and MLN cures have lower activation energies than that of commercial resin with 9 wt% HMTA, the usual proportion employed for industrial applications.

The kinetic parameters obtained for resin samples cured using each $g(\alpha)$ mechanism of the Coats and Redfern method are shown in Table 4. The application of this model was carried out using all experimental data. Thus, R^2 coefficients of the data fits for all curing processes are, in general, poor. The kinetic data for resin curing exhibit an acceptable fit for a two-dimensional nucleation mechanism, A₃ and A₄, particularly in the LN case. However, the results obtained from the application of Coats-Redfern's method are not in concordance with those obtained using Belichmeier, Ozawa and Kissinger's methods; with the exception of LN kinetic data generated using the A₂ conversion function. Therefore, the best conversion function in each case cannot be clearly determined using this method, as other authors have reported [36].

The Belichmeier, Ozawa and Kissinger's methods give a single value for the activation energy for the overall process. The kinetics of LN and MLN resin cures exhibit similar activation energy values. The values obtained for the studied system are in accordance with data in the literature for novolac curing kinetics [8, 17, 23, 37, 38]. These values are in the range of 100–120 kJ mol⁻¹.

Conclusions

In this work, three non-isothermal methods have been tested to explain the curing kinetics of several novolac resins, and a model-fitting method was applied to predict the reaction mechanism using a function, $g(\alpha)$. Belichmeier's method is straightforward and rapid. In the case of commercial novolacs, the activation energy obtained for the novolacs curing process is higher than values obtained for LN and MLN resins curing. Ozawa and Kissinger's methods give similar activation energy values. In addition, the incorporation of lignosulfonate, directly methylolated, does not exhibit a variation in the kinetic parameters of the process with respect to those of PF resin curing. The use of Coats-Redfern's method can be justified when the conversion function, $g(\alpha)$, chosen leads to results similar to those obtained using other methods.

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