

Thermal degradation of lignin–phenol–formaldehyde and phenol–formaldehyde resol resins

Structural changes, thermal stability, and kinetics

M. V. Alonso · M. Oliet · J. C. Domínguez ·
E. Rojo · F. Rodríguez

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Abstract Resol resins are used in many industrial applications as adhesives and coatings, but few studies have examined their thermal degradation. In this work, the thermal stability and thermal degradation kinetics of phenol–formaldehyde (PF) and lignin–phenol–formaldehyde (LPF) resol resins were studied using thermogravimetric analysis (TG) in air and nitrogen atmospheres in order to understand the steps of degradation and to improve their stabilities in industrial applications. The thermal stability of samples was estimated by measuring the degradation temperature (T_d), which was calculated according to the maximum reaction rate criterion. In addition, the ash content was determined at 800 °C in order to compare the thermal stability of the resol resin samples. The results indicate that 30 wt% ammonium lignin sulfonate (lignin derivative) as filler in the formulation of LPF resin improves the thermal stability in comparison with PF commercial resin. The activation energies of degradation of two resol resins show a difference in dependence on mass loss, which allows these resins to be distinguished. In addition, the structural changes of both resins during thermal degradation were studied by Fourier transform infrared spectroscopy (FTIR), with the results indicating that PF resin collapses at 300 °C whereas the LPF resin collapses at 500 °C.

Keywords Thermal stability · Phenolic resins · Lignin · Isoconversional analysis

Introduction

The manufacturing process of phenol–formaldehyde (PF) resins has remained unchanged for several decades. However, numerous efforts have been carried out to reduce the dependence of this industry on phenol, the cost of which is subject to fluctuations in the price of oil. Many researchers have presented as an attractive alternative the incorporation of natural polymers such as lignin, lignin derivative, and tannins in the formulation of phenolic resins [1–3]. These polymers are widely used in structural adhesives, coatings, and advanced composite matrices in aerospace and electronic industries because they offer high fire resistance, high char yield, and solvent resistance [4–6]. Therefore, thermal degradation of resol resins is an important research topic, specifically their heat resistance, thermal stabilization, and degradation kinetics.

Many attempts have been made to monitor the thermal degradation of phenol–formaldehyde (PF) resins using infrared spectroscopy (IR), pyrolysis–gas chromatography (Py-GC), mass spectrometry (MS), solid-state ^1H and ^{13}C NMR, and thermogravimetric analysis (TG). For instance, Tugtepe and Özgümüş [7] studied the influence of titanium and silicon on the oxidative degradation of phenolic novolac resins. Gao et al. [8] used FTIR to analyze the structural changes that phenolic resins undergo when degrading in the presence of boron in an air atmosphere. They found that the presence of boron retarded the degradation of the resin. Chen et al. [9] also studied the structural changes in phenolic materials undergoing degradation using FTIR and solid-state ^{13}C NMR in order to understand the reaction mechanism. Zárate et al. [10] used the TG technique to study the thermal stabilities of natural fibers, phenolic resoles, and the final reinforced composites. Despite these numerous studies, our understanding of

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

how phenolic resins degrade is controversial and incomplete, since the degradation follows more than one mechanism [11–14].

Kinetic characterization of the degradation of phenolic resins is important for understanding structural changes that occur during the different phases of degradation, which can help predict and improve the industrial performance of the resin. The literature contains different methods for determining the kinetic parameters of polymer degradation, including activation energies and pre-exponential factors. The model-fitting method (single- and multi-heating rate) and the isoconversional method are widely used to describe the behavior of materials in an inert or oxidative atmosphere using different thermal analysis techniques, such as thermogravimetry (TG), differential scanning calorimetry (DSC), and dynamic-mechanical analysis (DMA) [14–19]. In some cases, these methods provide a reasonably accurate description of the kinetics of degradation.

In this work, we used FTIR to identify and compare the structural changes during the thermal degradation of a commercial phenol–formaldehyde resin (PF) and a lignin–phenol–formaldehyde resin (LPF) containing 30 wt% of softwood ammonium lignin sulfonate (ALS). It should be noted that the study of LPF resin is an interesting alternative to replace phenol by lignin derivative in the formulation due to the low cost and low toxicity of this natural polymer. In addition, we determined the characteristic values of decomposition and thermal stability of PF and LPF resins by thermogravimetry under inert and

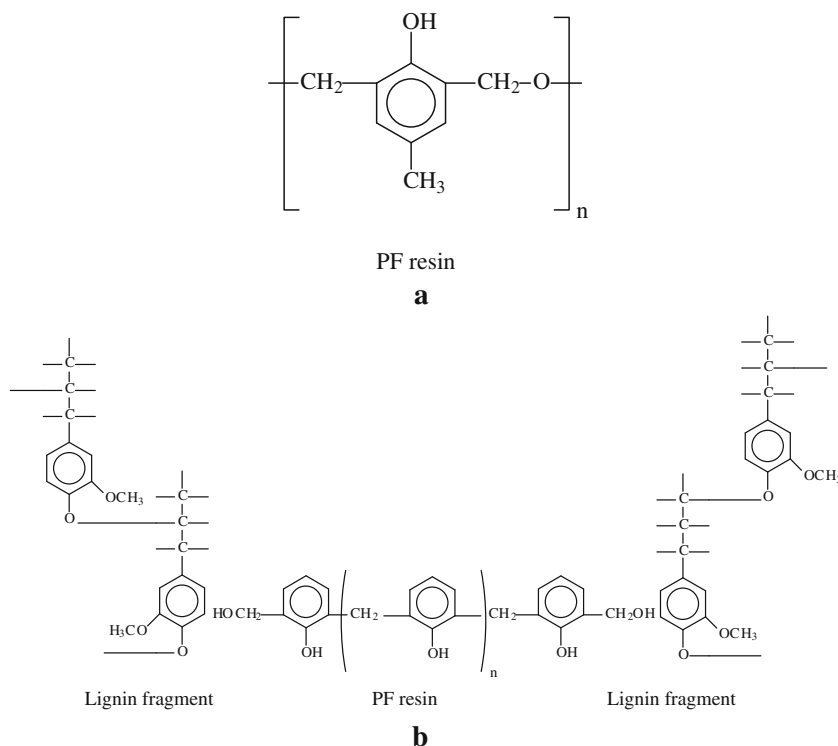
oxidative atmospheres. Finally, the Flynn–Wall–Ozawa method was used to describe the thermal degradation of both resol resins and to examine the dependence of activation energy on mass loss.

Experimental

Phenol–formaldehyde commercial resol (PF) resin tested was supplied by Hexion Specialty Chemical (Spain). The main properties of commercial resin were <0.2% free phenol content, 275–475 cP viscosity (25 °C), and 45–47% solids content. Lignin–phenol–formaldehyde resin (LPF) was synthesized with 30 wt% of ammonium lignin sulfonate as filler, which presented similar final properties to PF resin. Possible chemical structures of both resol resins are shown in Fig. 1. The softwood ammonium lignin sulfonate employed for the lignin-phenolic resin was provided by Borregaard Deutschland as Borresperse AM 320. The lignin sulfonate used in the present work was the ammonium salt, which has unlike all other commercial products lignin sulfonate salts is soluble in phenol. Note that the ALS used presents 5% ammonium, 2% ash, and 6% reducing sugars.

In each degradation experiment, 12 mg of PF or LPF was subjected to thermal degradation at a heating rate of 10 °C min⁻¹ in a TG apparatus (Mettler Toledo TGA 851^o). At specific times during the degradation, samples of the material were withdrawn and analyzed by FTIR (Mattson Satellite spectrophotometer). The acquisition conditions were as

Fig. 1 Chemical structures.
a Phenol–formaldehyde resin,
b lignin–phenol–formaldehyde resin



follows: spectral width, 4000–500 cm^{-1} ; 32 accumulations; gain, 2; resolution, 4 cm^{-1} ; and signal processing by triangular apodization. Band assignments were made according to the literature [9, 20, 21].

In addition, the degradation kinetics of the aforementioned resins were studied under both inert and oxidizing atmospheres using the Flynn–Wall–Ozawa method. Thus, non-isothermal TG runs were carried out at heating rates (β) of 4, 6, 8, 10, 12, 14, 16, and 20 $^{\circ}\text{C min}^{-1}$ in a 30–900 $^{\circ}\text{C}$ temperature range under an air or nitrogen atmosphere at a flow rate of 30 mL min^{-1} . Under inert atmosphere, to ensure there was no air in the equipment and to calibrate the analyzer, the apparatus was operated in nitrogen (purity, 99.9999%; atmospheric pressure) before the thermal decomposition process was performed. Average values for kinetic parameters of resin degradation process were determined from a minimum of three replicates.

Kinetic analysis

Isoconversional methods employed in this work are based on dynamic analysis using TG. In general, the reaction rate equation used to study the resin degradation kinetics can be expressed as:

$$\frac{dw}{dt} = k(T) \cdot f(w) \quad (1)$$

Considering that the rate equation (1) is valid for dynamic degradation and that $dw/dt = \beta(dw/dT)$, where β is the heating rate ($^{\circ}\text{C min}^{-1}$), and k is the rate constant expressed in the Arrhenius equation, which is a function of temperature, Eq. 1 can be written as:

$$\beta \cdot \frac{dw}{dT} = A \cdot e^{(-E/RT)} \cdot f(w) \quad (2)$$

where T is the temperature, A is the pre-exponential factor, E is the activation energy, which is independent of conversion, R is the gas constant, and w is the mass loss, which is defined by expression (3):

$$w = \frac{m_0 - m}{m_0 - m_{\infty}} \quad (3)$$

where m_0 is the initial mass of the sample, m is the sample mass for the reaction at time t , and m_{∞} is the final mass of the sample in the considered step. In this way, the integral form of the rate equation (Eq. 2) can be expressed as:

$$g(w) = \int_0^w \frac{dw}{f(w)} = \frac{A}{\beta} \int_0^{T_w} e^{(-E/RT)} dT = \frac{A}{\beta} P(E, T) \quad (4)$$

$P(E/RT)$ can be expressed in the 20–60 E/RT range as follows:

$$\log P(E/RT) = -2.315 - 0.4680 \cdot c \cdot E/RT, \quad (5)$$

where an initial value of $c = 1.052$ is used to calculate an activation energy, which is then used to recalculate c . This process is repeated by an iterative procedure to maximize the fit to the experimental data.

In order to determine the kinetic parameters of process, Eqs. 4 and 5 can be combined and rearranged as:

$$\log \beta_i = A' - 0.4567 \cdot \frac{E_w}{R \cdot T_{w,i}} \quad (6)$$

where $A' = \log(A \cdot E_w/g(w) \cdot R) - 2.315$. Expression (6) is known as the Flynn–Wall–Ozawa method [22, 23], which can be applied to different mass losses. Thus, for a given mass loss, according to Eq. 6, the activation energy and the constant A' can be calculated from the slope and the ordinate, respectively, of the linear relation between $\log \beta_i$ and $1/T_{w,i}$.

The precision of the integral methods can be improved by using numerical integration, which has been developed by Vyazovkin [24, 25]. In this work, the Flynn–Wall–Ozawa method is used to analyze the degradation kinetics.

Results and discussion

Structural changes of phenol–formaldehyde and lignin–phenol–formaldehyde resins during degradation

The structural changes in both resol resins residues subjected to heat treatment at different temperatures by TG under an oxidative atmosphere were established by FTIR (Fig. 2). The results show that the intensities and the bands of all functional groups changed with increasing temperature. The intensity of phenolic and methylol hydroxyl bands at 3620–3030 cm^{-1} decreased significantly and became narrower with high temperatures (≥ 500 $^{\circ}\text{C}$) due to the decrease in the number of hydroxyl groups [26]. Carbonyl groups normally appear at 1650 cm^{-1} as a shoulder peak on the 1600 cm^{-1} (aromatic C–C stretch). When the temperature was increased, the signal intensity of the carbonyl groups decreased. Hydroxymethyl groups (1010 cm^{-1}) were stripped in the first stage of degradation [26]. The band at 1060 cm^{-1} decreased, indicating the loss of aliphatic alcohols during heating. It should also be noted that the peak at 1480 cm^{-1} , which is ascribed to the absorption of methylene (CH_2) bridges, decreased sharply in the PF resin, while it increased for the LPF resin; in contrast, the intensity of aliphatic CH_3 at 1437 cm^{-1} increased for both resins [9, 27]. This change in the commercial resin indicates that the LPF resin has higher thermal stability. Thus, when the methylene bridges decomposed, the resin's structure collapsed. This may explain why the char yield of PF resin was lower than that

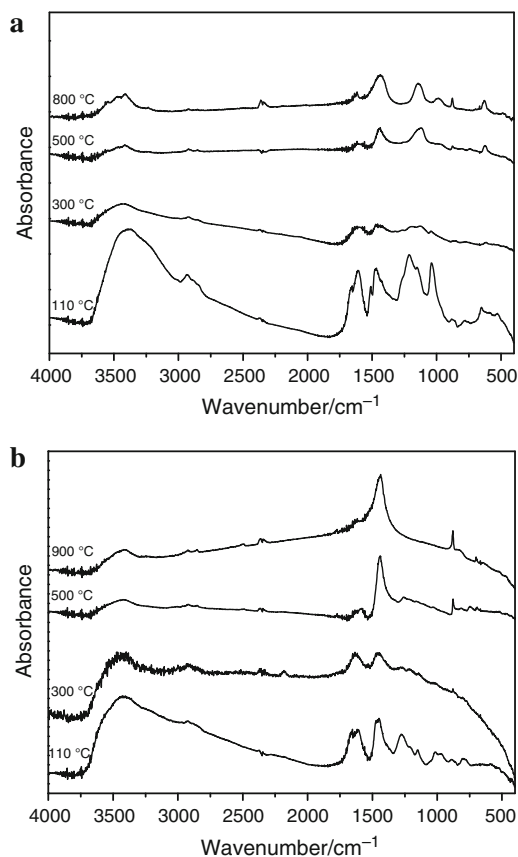


Fig. 2 FTIR spectra at different degradation temperatures under an oxidant atmosphere. **a** LPF resin, **b** PF resin

of lignin–phenol–formaldehyde resin, which has been determined by a new set of TG experiments.

Figure 3 shows the structural changes in the PF and LPF resin residues heat-treated at different temperatures under an inert atmosphere. It should be noted that the spectra of both resins show more rapid decomposition with increasing temperature under an inert atmosphere than under oxidative conditions. In the phenolic resins, the majority of the bands disappeared when the temperature reached 300 °C, while the absorption bands of the lignin–phenolic resin only decreased in intensity. Thus, the phenolic O–H stretching band at 3410 cm^{-1} in the phenolic resin decreased, and the alcoholic OH groups were decomposed into carbonyl groups (1650 cm^{-1}) [9]. The broadness of this band is due to the overlap with the stretching aromatic C–C band (1600 cm^{-1}). The peak at 1466 cm^{-1} , ascribed to the methylene bridges, disappeared when the temperature was increased to 500 °C. The structure of the PF resin began to degrade through dehydrogenation and carbonization reactions at 300 °C. The structural changes during the degradation of LPF resin were similar to those of the PF resin; however, the structure of lignin–phenolic resin collapsed at 500 °C. Thus, the LPF resin shows higher

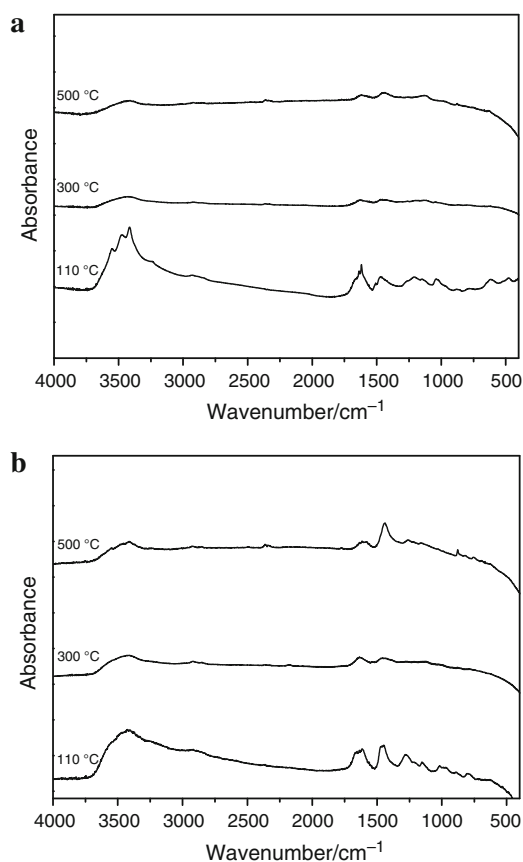


Fig. 3 FTIR spectra at different degradation temperatures under an inert atmosphere. **a** LPF resin, **b** PF resin

resistance to thermal degradation than that of the commercial resin.

Thermal stability

We focused first on the thermal stability of PF and LPF resin resins under an oxidative atmosphere. The measurements of the amount and rate (velocity) of change in the mass (mass loss) of a sample as a function of temperature or time in a controlled atmosphere are used primarily to determine the oxidative stabilities of materials as well as their compositional properties. The TG technique can analyze materials that exhibit mass loss due to decomposition, oxidation and/or loss of volatiles (such as moisture). We found that the degradation of resin resins occurs in four steps, as it is shown in the TG/DTG curves obtained with a heating rate of 10 $^{\circ}\text{C min}^{-1}$ (Fig. 4). In the first stage, the LPF resin began to cure, and some monomers of low molecular weight were released at 62.6 °C, while the PF resin presented the emission of volatiles at 74.7 °C. This fact indicates that commercial resin has monomers with a higher molecular weight than those of the LPF resin.

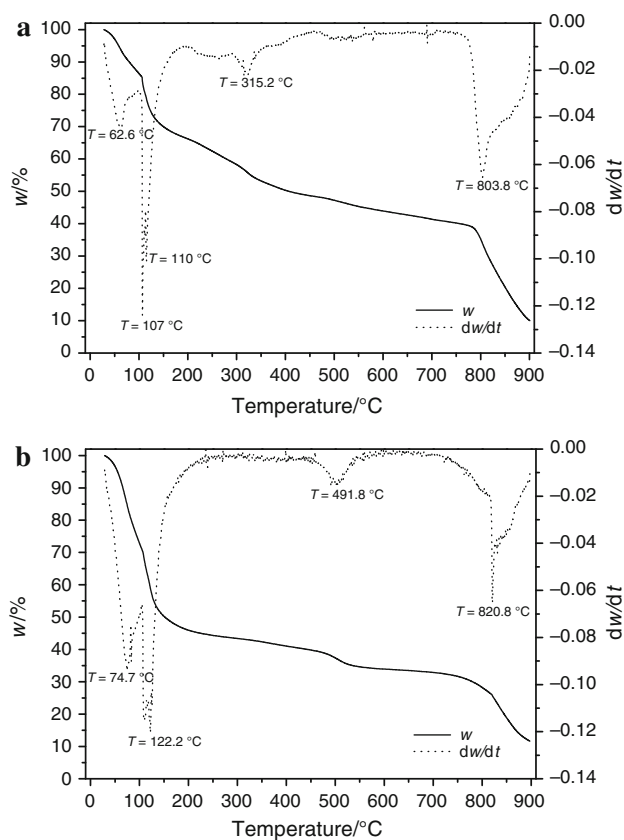


Fig. 4 TG/DTG curves at $10\text{ }^{\circ}\text{C min}^{-1}$ under an oxidant atmosphere. **a** LPF resin, **b** PF resin

In the second stage of degradation, the LPF resin showed a sharp double peak due to the evaporation of water and the appearance of volatiles at 107 and 110 °C, respectively. However, the PF resin showed a broad peak at $\sim 122\text{ }^{\circ}\text{C}$ as a result of a diffusion barrier arising during the first condensation reactions in the system [28]. It is well known that the mass loss of phenolic resin during post-curing is $\sim 15\%$ [28, 29]. The analyzed PF and LPF resins showed mass losses of 11.5 and 20%, respectively, which is in accordance with the literature on thermal degradation of phenolic resins. In the case of the LPF resin, the mass loss value was high due to the degradation of side chains of the ammonium lignin sulfonate. Khan and Ashraf [29] also observed that a higher mass loss for phenol–formaldehyde resins with incorporation of lignin sulfonate may be a consequence of the degradation of side chains of the lignin molecules.

The third stage of degradation is due to the thermo-oxidation of the resol resin samples. During this step, the PF and LPF resins were degraded, with mass losses of 21.3 and 31.2 wt%, respectively. The mass percentage lost was due to the loss of methylene and water fragments, which left a char residue [28]. In the final stage of process, the PF and LPF samples were completely degraded.

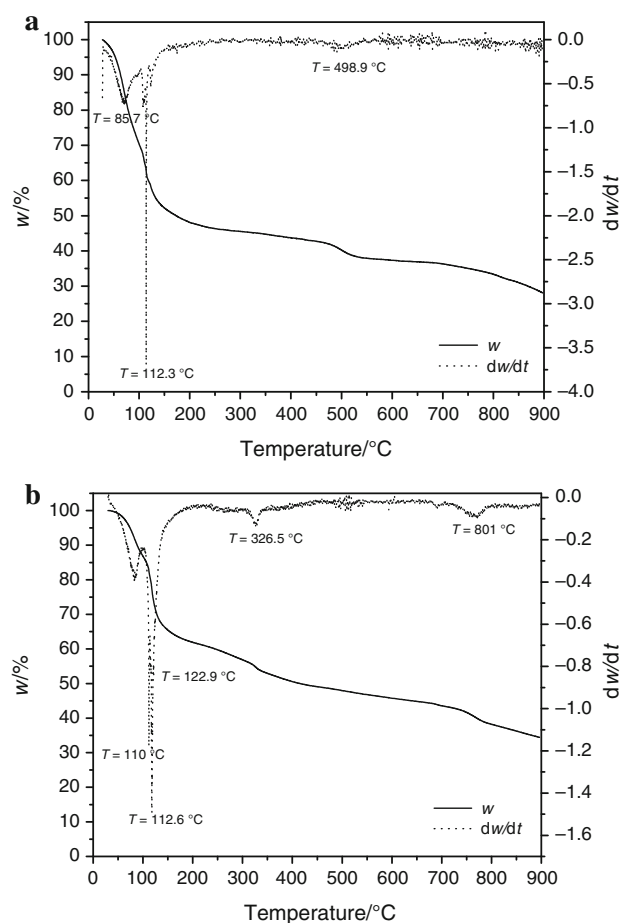


Fig. 5 TG/DTG curves at $10\text{ }^{\circ}\text{C min}^{-1}$ under an inert atmosphere. **a** LPF resin, **b** PF resin

In contrast to these four steps observed for resin degradation in an oxidative atmosphere, the analysis of the thermal stability of PF and LPF resol resins under an inert atmosphere using TG/DTG curves at $10\text{ }^{\circ}\text{C min}^{-1}$ showed degradation in three steps (Fig. 5). As mentioned before, the change of mass (mass loss) for resins as a function of temperature or time in a controlled atmosphere allows determining the thermal stabilities of materials as well as their compositional properties. In the first stage, the LPF resin began to cure, and some monomers of low molecular weight were released at 85.7 °C, while the PF resin showed the emission of volatiles at 72.1 °C. In this stage, the results attained for the commercial resin were similar to those obtained under an oxidative atmosphere. However, the temperature of stability for LPF resin rose from 62.6 °C in air to 85.7 °C in nitrogen because the resin sample was more stable under inert conditions; therefore, the emission of volatiles was delayed. In the second stage, the LPF resin showed a sharp double peak due to water evaporation and to diffusion barriers at 112.3 and 118.2 °C, respectively. However, the PF resin exhibited a peak at 110 °C as a

result of water evaporation. This peak presented two shoulders at 112.6 and 122.9 °C due to the evaporation of volatiles and to the appearance of a diffusion barrier during the first condensation reactions in the system, similar to the corresponding step under an oxidative atmosphere. The mass losses of phenolic and lignin-phenolic resins during post-curing were ~19 and 26%, respectively; the value for LPF resin is higher than for PF resin and other phenolic systems previously reported [8, 29]. In the case of the LPF resin, the mass loss value was high due to the degradation of side chains of the ALS, as discussed previously. The third stage was due to the thermal degradation of hydrocarbon chains of the resol resin samples. During this step, the PF and LPF resins were completely degraded, with mass losses of 21.3 and 31.2 wt%, respectively.

Under the operating conditions (inert or oxidant atmospheres) studied, what are occurring with the sulfonate groups and the presence of ionic ammonium group? As is well known, the main reaction of lignin sulfonate, under alkaline media, are desulfonation, phenol and self-condensation, often accompanied by reverse aldol condensation. In this work, the desulfonation of lignin sulfonate is easily produced upon alkaline hydrolysis [30]. The sulfonate group is an excellent leaving group for being a weak base, and the substitution of α -sulfonic acid with a hydroxyl group takes place during the thermal degradation of polymer in alkaline media, followed by decomposition of sulfonic acid functional groups releasing SO₂ [31]. The ammonium group is transformed as ammonia in the early stages of degradation to the extent that the sulfonic group is also degraded.

Finally, higher ash content indicates that a polymer is more thermally stable. Phenolic resin with ammonium lignin sulfonate as filler showed higher thermal stability than the commercial sample under oxidative and inert atmospheres. This fact is also shown in Figs. 4 and 5, where the contents of ash for the PF and LPF resins, measured at 800 °C, were 28 and 36 wt% in *air* and 31 and 38 wt% in *nitrogen*, respectively. A high content of ash for the lignin-phenolic resin is in accordance with the results obtained by FTIR, as described above.

Thermo-oxidation kinetics

The isoconversional method, described in Eq. 6, was applied to different percentages of mass loss (w) from resins during their degradation (third stage, Fig. 4). According to this equation, for each mass loss, the logarithm of the heating rate correlates inversely with temperature. The obtained results of activation energy, pre-exponential factor A' , and the correlation coefficients are exhibited in Table 1. The obtained values using the Flynn–

Table 1 Kinetic parameters and correlation coefficients of the thermal degradation of PF and LPF resol resins under oxidant and inert atmospheres by Flynn–Wall–Ozawa method

| w/% | PF | | | LPF | | |
|----------------------------|--------------------------|-------|-------|--------------------------|-------|-------|
| | $E_w/\text{kJ mol}^{-1}$ | A' | R^2 | $E_w/\text{kJ mol}^{-1}$ | A' | R^2 |
| <i>Air atmosphere</i> | | | | | | |
| 2 | 110.5 | 21.13 | 0.969 | 101.3 | 10.93 | 0.978 |
| 5 | 108.2 | 22.11 | 0.970 | 104.3 | 11.18 | 0.972 |
| 10 | 115.6 | 23.65 | 0.965 | 109.4 | 11.61 | 0.953 |
| 20 | 124.4 | 25.55 | 0.938 | 118.2 | 12.32 | 0.884 |
| 30 | 132.8 | 21.03 | 0.879 | 123.4 | 12.65 | 0.881 |
| 40 | 139.2 | 23.19 | 0.871 | 122.0 | 12.40 | 0.841 |
| 50 | 146.4 | 28.18 | 0.857 | 123.8 | 12.47 | 0.771 |
| 60 | 157.9 | 30.90 | 0.692 | 127.9 | 12.69 | 0.873 |
| 70 | 137.3 | 18.40 | 0.943 | 114.4 | 11.33 | 0.781 |
| 80 | 143.0 | 18.25 | 0.983 | 99.7 | 9.87 | 0.652 |
| 90 | 124.0 | 14.77 | 0.891 | 85.1 | 8.44 | 0.506 |
| 95 | 154.3 | 20.97 | 0.836 | 77.1 | 7.68 | 0.428 |
| 98 | 145.6 | 19.68 | 0.862 | 72.4 | 7.23 | 0.381 |
| 100 | 143.8 | 19.33 | 0.875 | 30.6 | 3.65 | 0.105 |
| <i>Nitrogen atmosphere</i> | | | | | | |
| 2 | 68.9 | 16.90 | 0.982 | 142.1 | 17.26 | 0.977 |
| 5 | 69.4 | 16.54 | 0.988 | 139.5 | 17.26 | 0.979 |
| 10 | 69.5 | 16.52 | 0.981 | 136.9 | 17.40 | 0.980 |
| 20 | 67.7 | 16.95 | 0.953 | 134.8 | 17.52 | 0.967 |
| 30 | 70.1 | 17.98 | 0.927 | 137.6 | 17.79 | 0.944 |
| 40 | 84.4 | 18.37 | 0.906 | 144.4 | 17.83 | 0.927 |
| 50 | 112.0 | 18.17 | 0.891 | 156.9 | 17.33 | 0.918 |
| 60 | 139.6 | 18.07 | 0.875 | 177.6 | 17.14 | 0.886 |
| 70 | 158.6 | 18.56 | 0.857 | 180.9 | 15.92 | 0.825 |
| 80 | 189.9 | 19.61 | 0.914 | 182.1 | 14.65 | 0.748 |
| 90 | 208.0 | 18.39 | 0.802 | 177.9 | 13.37 | 0.664 |
| 95 | 208.9 | 21.55 | 0.855 | 176.2 | 12.83 | 0.627 |
| 98 | 211.2 | 23.30 | 0.984 | 175.5 | 12.51 | 0.606 |
| 100 | 210.9 | 17.89 | 0.692 | 175.0 | 12.27 | 0.585 |

R^2 correlation coefficient

Wall–Ozawa method for the activation energy of both resins are shown in Fig. 6.

The variation in the activation energy of process with the mass loss for the two systems indicates that the resin degradation is a complex mechanism. In the first step of resin degradation, which involved up to 30 wt% mass loss, LPF resin showed a slight build-up of activation energy. Between losses of 30 and 60 wt%, the activation energy remained constant ($E_w \sim 120 \text{ kJ mol}^{-1}$) for the lignin-phenol-formaldehyde resin degradation. However, the activation energy for the phenol-formaldehyde resin process increased for mass losses of up to 60 wt%, when the value was $\sim 160 \text{ kJ mol}^{-1}$. It is important to note that the activation energy of the phenolic resin degradation varied

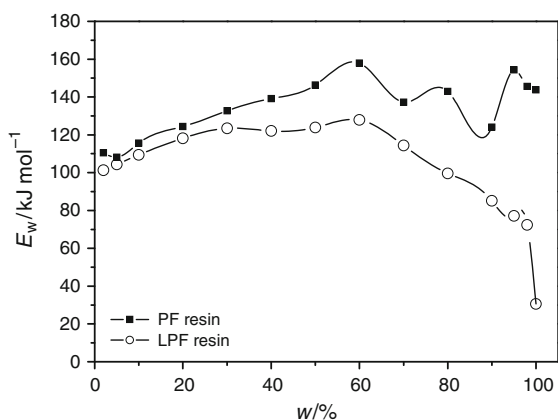


Fig. 6 Variation of activation energy as a function of mass loss for PF and LPF resins under an oxidant atmosphere

significantly in the third stage of process ($w > 60$ wt%) due to competing reactions [32]. Thus, the PF resin is degraded and cross-linked at the same time. In the case of LPF resin, the activation energy values decreased by 30 kJ mol^{-1} when mass loss was greater than 60 wt%. The rapid decrease of activation energy for LPF resin degradation may indicate that the overall process rate is diffusion-limited [30]. The values of activation energy for LPF resin decomposition are in accordance with results for powder coating of polyester and hybrid systems of epoxy-polyester [19].

Thermal degradation kinetics under a nitrogen atmosphere

This section uses the Flynn–Wall–Ozawa method to present an isoconversional kinetic analysis of the degradation data for resin samples studied under an inert atmosphere (Table 1). The analysis of the dependence of the activation energy of degradation on the extent of degradation (w) provides information on how the polymer structure affects the degradation kinetics. The data on activation energy versus the extent of degradation for LPF and PF resins are shown in Fig. 7. During the early steps of the decomposition of LPF and PF resins ($w \leq 30$ wt%), the activation energy remained constant at 140 and 70 kJ mol^{-1} , respectively. This result suggests that the initial degradation is due to the breaking of the weakest linkages, whose concentrations are high [33].

For greater mass losses ($30 \text{ wt}\% < w < 60 \text{ wt}\%$), the activation energy for the LPF resin increased from ~ 140 to 180 kJ mol^{-1} . In the case of the commercial resin, the activation energy increased up to $\sim 200 \text{ kJ mol}^{-1}$ ($w = 90 \text{ wt}\%$). The high values of activation energy indicate the degradation of the main network bonds of the PF resin. In addition, the greater increase in the activation

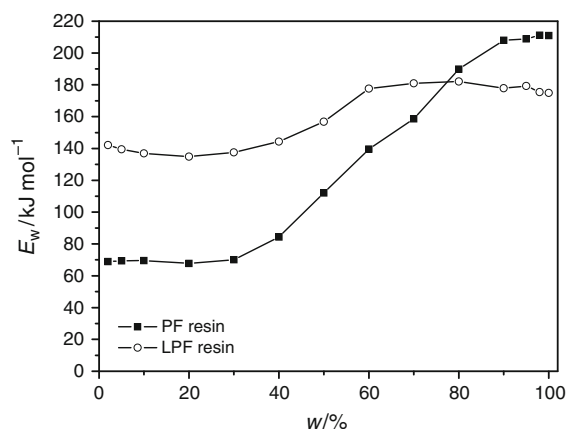


Fig. 7 Variation of activation energy as a function of mass loss for PF and LPF resins under an inert atmosphere

energy in the case of the PF resol resin can be due to the fact that its structure is more ordered than that of the LPF resin, which requires less energy to break than the structure of the commercial resin. Finally, for both resins, the activation energies remain at a constant value in the final step of their degradations.

Our findings show that changing the reaction medium alters the dependence of the activation energy on the extent of degradation for both resins. Even with this heterogeneity, the isoconversional analysis provides an interpretation of the behavior of both resins during their degradation. This methodology can be extended to the study of thermal degradation of other complex polymer systems.

Conclusions

The kinetics and mass loss during thermal decomposition of phenol–formaldehyde and lignin–phenol–formaldehyde resol resins have been studied in both oxidative and inert atmospheres using thermogravimetry. In addition, the structural changes of both resin types during degradation have been analyzed using FTIR. The results allow correlating the differences between the chemical structures of LPF and PF resins during their degradation processes, which may prove useful for understanding how each resin can best be applied in industrial settings.

The desulfonation reaction is produced for the degradation of LPF resin under alkaline conditions for both atmospheres studied—inert and oxidant—producing the decomposition of sulfonic acid functional groups releasing SO_2 . The ammonium group of lignin sulfonate is transformed as ammonia in the early stages of degradation. Although the degradation temperatures and ash contents of PF and LPF resins were within the acceptable range, the thermal stability of the LPF resin samples was superior in

relation to commercial resin. The variation of activation energy with temperature was different for lignin-phenolic resin than for commercial resin, indicating that the degradation mechanism of the resin samples changes under different atmospheres. Overall, the results seem to indicate that under inert atmosphere, the collapse of PF resin (300 °C) occurs before that of the LPF resin (500 °C).

While this study provides important insights into the degradation mechanism of the two resins, it would be useful to apply more complex kinetic methods to study their degradation. In addition, the approach described in the present work could be applied to the kinetic study of thermal degradation of other polymers.

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References

- Alonso MV, Oliet M, Rodriguez F, Astarloa G, Echeverria JM. Use of a methylolated softwood ammonium lignosulfonate as partial substitute of phenol in resol resins manufacture. *J Appl Polym Sci.* 2004;94(2):643–50.
- Benar P, Gonçalves AR, Mandelli D, Schuchardt U. Eucalyptus organosolv lignins: study of the hydroxymethylation and use in resols. *Bioresour Technol.* 1999;68(1):11–6.
- Olivares M, Aceituno H, Neiman G, Rivera E, Sellers TJ. Lignin-modified phenolic adhesives for bonding radiata pine plywood. *For Prod J.* 1995;45(1):63–7.
- Cho D, Il Yoon B. Microstructural interpretation of the effect of various matrices on the ablation properties of carbon-fiber-reinforced composites. *Compos Sci Technol.* 2001;61(2):271–80.
- Mao J, Chang J, Chen Y, Fang D. Review of phenolic foam. *Ind Eng Chem Res.* 1998;15(3):38–43.
- Mouritz AP. Post-fire flexural properties of fibre-reinforced polyester, epoxy and phenolic composites. *J Mater Sci.* 2002; 37(7):1377–86.
- Tugtepe M, Özgümüş S. Modified phenol-formaldehyde novolac resins: synthesis and thermal oxidative degradation. *J Appl Polym Sci.* 1990;39(1):83–101.
- Gao J, Xia L, Liu Y. Structure of a boron-containing bisphenol-F formaldehyde resin and kinetics of its thermal degradation. *Polym Degrad Stabil.* 2004;83(1):71–7.
- Chen Y, Chen Z, Xiao S, Liu H. A novel thermal degradation mechanism of phenol-formaldehyde type resins. *Thermochim Acta.* 2008;476(1–2):39–43.
- Zárate CN, Aranguren MI, Reboredo MM. Thermal degradation of a phenolic resin, vegetable fibers, and derived composites. *J Appl Polym Sci.* 2008;107(5):2977–85.
- Budrugaec P, Segal E. Application of isoconversional and multivariate non-linear regression methods for evaluation of the degradation mechanism and kinetic parameters of an epoxy resin. *Polym Degrad Stabil.* 2008;93(6):1073–80.
- Looyeh MRE, Samanta A, Jihan S, McConnachie J. Modelling of reinforced polymer composites subject to thermo-mechanical loading. *Int J Numer Meth Eng.* 2005;63(6):898–925.
- Núñez-Regueira L, Villanueva M, Fraga-Rivas I. Activation energies for the thermodegradation process of an epoxy-diamine system. *J Therm Anal Calorim.* 2006;83(3):727–33.
- Zhang Z, Gu A, Liang G, Ren P, Xie J, Wang X. Thermo-oxygen degradation mechanisms of POSS/epoxy nanocomposites. *Polym Degrad Stabil.* 2007;92(11):1986–93.
- Alonso MV, Oliet M, Garcia J, Rodriguez F, Echeverria J. Transformation of dynamic DSC results into isothermal data for the curing kinetics study of the resol resins. *J Therm Anal Calorim.* 2006;86(3):797–802.
- Alonso MV, Oliet M, Garcia J, Rodriguez F, Echeverria J. Gelation and isoconversional kinetic analysis of lignin-phenol-formaldehyde resol resins cure. *Chem Eng J.* 2006;122(3):159–66.
- Alonso MV, Oliet M, Pérez JM, Rodríguez F, Echeverría J. Determination of curing kinetic parameters of lignin-phenol-formaldehyde resol resins by several dynamic differential scanning calorimetry methods. *Thermochim Acta.* 2004;419(1–2):161–7.
- Kandare E, Kandola BK, Staggs JEJ. Global kinetics of thermal degradation of flame-retarded epoxy resin formulations. *Polym Degrad Stabil.* 2007;92(10):1778–87.
- Morancho JM, Salla JM, Ramis X, Cadenato A. Comparative study of the degradation kinetics of three powder thermoset coatings. *Thermochim Acta.* 2004;419(1–2):181–7.
- Rao M, Alwan S, Scariah K, Sastri K. Thermochemical characterization of phenolic resins. *J Therm Anal Calorim.* 1997;49(1): 261–8.
- Roczniak K, Biernacka T, Skarżyński M. Some properties and chemical structure of phenolic resins and their derivatives. *J Appl Polym Sci.* 1983;28(2):531–42.
- Flynn JH, Wall LA. General treatment of the thermogravimetry of polymers. *J Res NBS A Phys Chem.* 1966;70(6):487–523.
- Ozawa T. A new method of analyzing thermogravimetric data. *Bull Chem Soc Jpn.* 1965;38(11):1881–6.
- Vyazovkin S. Evaluation of activation energy of thermally stimulated solid-state reactions under arbitrary variation of temperature. *J Comput Chem.* 1997;18(3):393–402.
- Vyazovkin S. Modification of the integral isoconversional method to account for variation in the activation energy. *J Comput Chem.* 2001;22(2):178–83.
- He G, Riedl B. Curing kinetics of phenol formaldehyde resin and wood-resin interactions in the presence of wood substrates. *Wood Sci Technol.* 2004;38(1):69–81.
- Lee YK, Kim DJ, Kim HJ, Hwang TS, Rafailovich M, Sokolov J. Activation energy and curing behavior of resol- and novolac-type phenolic resins by differential scanning calorimetry and thermogravimetric analysis. *J Appl Polym Sci.* 2003;89(10):2589–96.
- Siimer K, Kaljuvee T, Christjanson P, Pehk T, Saks I. Effect of alkylresorcinols on curing behaviour of phenol-formaldehyde resol resin. *J Therm Anal Calorim.* 2008;91(2):365–73.
- Khan M, Ashraf S. Studies on thermal characterization of lignin. *J Therm Anal Calorim.* 2007;89(3):993–1000.
- Mathur VK. Characterization of spent sulphite liquor-phenol condensation. Thesis, University of Washington, SD121 TH30187 (1982).
- Singare PU, Lokhande RS, Madyal RS. Thermal degradation studies of polystyrenesulfonic and polyacrylic carboxylic cationites. *Russ J Gen Chem.* 2010;80(3):527–32.
- Vyazovkin S, Wight CA. Kinetics in solids. *Annu Rev Phys Chem.* 1997;48:125–49.
- Achiliadis DS, Karabela MM, Sideridou ID. Thermal degradation of light-cured dimethacrylate resins: Part I. Isoconversional kinetic analysis. *Thermochim Acta.* 2008;472(1–2):74–83.