

CHARACTERIZATION OF ALKALINE LIGNINS FOR USE IN PHENOL-FORMALDEHYDE AND EPOXY RESINS

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Besides polyurethanes and polyesters, phenolic and epoxy resins are the most prominent applications for technical lignins in thermosetting materials. To evaluate the potential application of lignin raw materials in phenol formaldehyde and epoxy resins, three types of alkaline lignins were characterized in terms of their structures and thermal properties. The lignin samples analyzed were kraft lignin (LIG-1), soda-rice straw lignin (LIG-2), and soda-wheat straw lignin (LIG-3). FTIR and ¹H-NMR methods were used to determine their structure. Gel permeation chromatography (GPC) was used to determine the molecular weight distribution (MWD). Differential scanning calorimetry (DSC) was used to measure the glass transition temperature (*T*_g), and thermogravimetric analysis (TGA) to determine the thermal stability of lignin samples. Results showed that kraft lignin (LIG-1) has moderate hydroxyl-group content, is rich in G-type units, and has good thermal stability. These properties make it more suitable for direct use in phenol formaldehyde resins, and it is therefore a good raw material for this purpose. The alkaline soda-rice straw lignin (LIG-2) with a high hydroxyl-group content and excellent thermal stability is most suited to preparing lignin-based epoxy resins.

Keywords: Alkaline lignin; Biomaterials; Characterization; Phenol formaldehyde; Epoxy resin

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INTRODUCTION

Lignin is the second most abundant natural polymer after cellulose. It is an amorphous and phenolic polymer that is present in large amounts in plant cells and wood tissues. Lignin is biosynthesized from the radical coupling reactions of three primary monolignol precursors: the coniferyl, sinapyl, and p-coumaryl alcohols, which lead, respectively, to guaiacyl (G), syringyl (S), and p-hydroxyphenyl (H) units (see Fig. 1). This process produces a polydisperse polymer with no extended sequences of regularly repeating units, which are linked by a multitude of interunit linkages that includes several types of ether (β -O-4, α -O-4, 4-O-5) and carbon-carbon linkages (Dence 1992). Thus, it is a complex and heterogeneous polymer. The heterogeneity of lignin is caused by the variation in composition, size, cross-linking, and functional groups, and it depends on the species of plant from which it is obtained, the pulping process used to separate it from cellulose, and the means by which it is recovered from the pulping liquor (Vazquez et al. 1997).

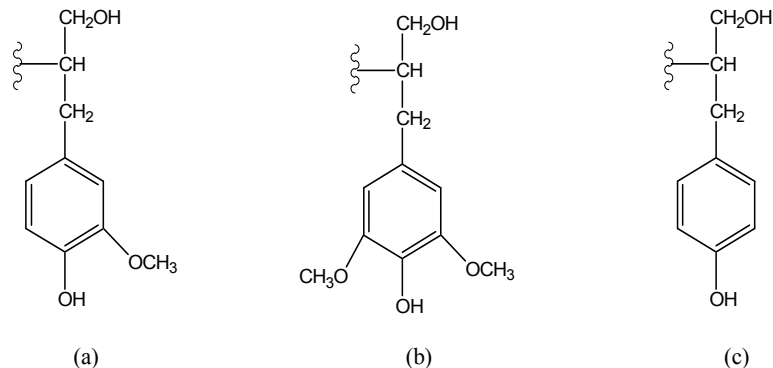


Fig. 1. Schematic representation of the structural units of lignin: (a) guaiacyl (G), (b) syringyl (S), (c) *p*-hydroxyphenyl propane (H)

Worldwide more than 50 million tons of lignin is being produced annually as residue in paper and ethanol production processes (Gosselink et al. 2004). With present technical knowledge and the existing technical characteristics of lignin products, this amount could be efficiently used to replace fossil resources but, instead, most lignins are burned to generate energy for pulp mills. Views, however, are now changing, and industry is beginning to show considerable interest in employing applications that use more environmentally friendly and natural compounds: for example, biomaterials, fuels, biocides and biostabilisers, animal feed health products, and crop cultivations (Lora and Glasser 2002).

In the field of biomaterials, lignin has been used to synthesize phenolic, polyester, polyurethane, and epoxy resins (Pizzi 1994; Alonso et al. 2004; Thring et al. 1997; Stewart 2008; Nonaka et al. 1997). Lignin is of interest especially in phenolic and epoxy resins because of its chemical structure, which is similar to that of phenol, which makes it a viable alternative to phenolic compounds in these resins. Lignin has been extensively investigated as a replacement for phenol in the synthesis of lignin-phenol-formaldehyde resin (Alonso et al. 2004; Benar et al. 1999; Danielson and Simonson 1998; Peng and Riedl 1994; Vazquez et al. 1995), and many researchers have developed methods for synthesizing lignin-based epoxy resins (Nonaka et al. 1997; Feldman et al. 1991a,b; Malutan et al. 2008; Simionescu et al. 1993; Sun et al. 2007; Ismail et al. 2010). In both cases, the properties of the final resins depend on the physico-chemical characteristics of lignin and, therefore, decisions on the suitability of using lignin in such applications require prior investigation of its chemical, structural, and thermal characteristics.

In this paper, three different alkaline lignins—namely kraft lignin (LIG-1), soda-rice straw lignin (LIG-2), and soda-wheat straw lignin (LIG-3)—were characterized for use in phenol formaldehyde and epoxy resins. The lignin samples were characterized both structurally and thermally by FTIR spectroscopy, ¹H-NMR spectroscopy, gel permeation chromatography (GPC), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA).

EXPERIMENTAL

Raw Materials

The alkaline lignins used in this study were obtained from the traditional kraft pulping process and the soda pulping process. Kraft lignin (LIG-1) was purchased from Sigma-Aldrich and used as received. Soda–rice straw lignin (LIG-2) was supplied by the South China University of Technology, Guangzhou, China. This lignin was produced by the ShangDong QuanMing Paper Making Co. Ltd. using the alkaline process with sodium hydroxide and Na_2CO_3 from rice straw. Soda-wheat straw lignin (LIG-3) was supplied by Luohe Huadong Lignin Co., Ltd., Henan, China. The LIG-2 and LIG-3 were purified according to the method reported by Lin (1992). They were treated with sulfuric acid (1%) several times and washed extensively with hot water to solubilize the residual sugars. These lignins are ash-free and have less than 0.5% sugar content. They were air-dried at room temperature to the equilibrium moisture content and stored in plastic bottles before they were characterized by the analytical methods described below. Other used reagents and solvents were analytic grade.

Structural Characterization and Molecular Weight Distribution

FTIR spectroscopy for lignins

The FTIR spectra of the lignin samples embedded in a KBr disk were obtained with a Nicolet 5700 FTIR-spectrophotometer using a resolution of 4 cm^{-1} and 32 co-addition scans in a frequency range of 400 to 4000 cm^{-1} . The pellet was prepared with a mixture of 300 mg potassium bromide and 5 mg of lignin samples. The spectra of the three alkaline lignins were analyzed by Nicolet software, and the absorbances of the functional groups were compared. The absorption bands were assigned as suggested by Faix (1992).

Proton nuclear magnetic resonance spectroscopy of acetylated lignins

The lignin samples were acetylated using the Thring et al. method (1991). Briefly, 30 mL of a 1:1 (v/v) mixture of pyridine and acetic anhydride was added to 2 g of lignin in a 100 mL conical flask, and, after stirring for 48 h at room temperature, the mixture was treated with 10-fold volumes of 1 % HCl at 0 °C. The resulting precipitate was filtered, washed with distilled water to neutral pH, and dried at room temperature.

Nuclear magnetic resonance spectroscopy was used to analyze the acetylated lignin samples. The ^1H -NMR spectra of 10 mg acetylated lignin samples dissolved in 0.5 mL of CDCl_3 were recorded on a Bruker AVANCE at 500 MHz using tetramethylsilane as internal standard. The proton signals were integrated from baseline and referred to the integrated signal of the methoxyl protons for the proton quantification of each functional group in the lignin molecule (Lundquist et al. 1980).

Phenolic hydroxyl groups by ultraviolet-spectroscopy ($\Delta\epsilon$ method)

The content of phenolic hydroxyl groups was determined as the total content of the phenolic hydroxyl units of lignin samples (see Fig.2) by UV-spectroscopy as described by Zakis (1994). This method is based on the difference in absorption at 300 and 360 nm between phenolic units in neutral and alkaline solutions. The content of

ionizing phenol hydroxyl groups can be quantitatively evaluated by comparing the $\Delta\varepsilon$ values of substance studied at certain wavelengths to the values of $\Delta\varepsilon$ of the respective model compounds (I, II, III, IV types, Fig. 1).

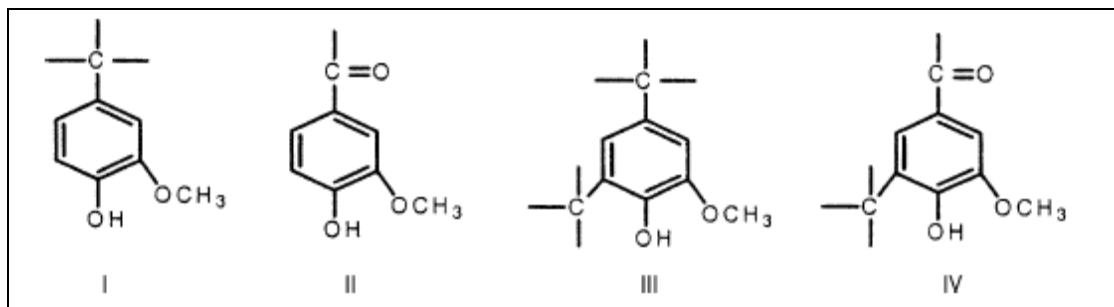


Fig. 2. Types of phenolic structures determined in different lignin samples.

Molecular weight distribution

The molecular weight of acetylated lignins was studied by gel permeation chromatography (GPC) equipped with three Waters Styragel HR345 Columns for THF packed with a high performance, fully porous, highly crosslinked styrene–divinylbenzene copolymer gel of 7.6 mm * 300 mm, supplied by Waters Co. The effluent was monitored with a Waters RI2414 RI-detector. The testing temperature was 35°C, and the injection volume was 100 μ L. The columns were calibrated using polystyrene standards in the 92–4.000.000 g/mol range. The THF flow was 1 mL/min, and the samples were dissolved in THF at a concentration of 1 mg/mL and stored for 24 h at 5 °C to avoid any variation in molecular weight (Glasser et al. 1993). The signal detected was digitized at a frequency of 2 Hz, and the MWD was calculated from the recorded signal using normal GPC calculation procedures (Yau et al. 1979).

Thermal Analysis

Differential scanning calorimetry (DSC)

Glass transition temperatures (T_g) were determined using a thermal analyzer TA MDSC2910. The DSC scans were recorded at a heating rate of 10 °C/min under nitrogen atmosphere with a flow rate of 60 mL/min. About 6 \pm 2 mg of sample was used in each test after drying for one day at 60°C under vacuum to eliminate water. The glass transition temperature (T_g) was defined as the mid point of the temperature range in which the change in heat capacity occurs.

Thermogravimetric analysis (TGA)

The thermal stability of the lignin samples was measured using a NETZSCH STA 409 PC/PG instrument operating from 25°C to 800°C at 10°C/min under a nitrogen atmosphere. TGA analysis measures the weight change of the sample as a function of temperature or time. The first derivative of the TG curve for the rate of mass loss vs temperature may be used to determine a single thermal decomposition temperature and compare the thermal characteristics of polymeric materials.

RESULTS AND DISCUSSION

FTIR Spectroscopy for Lignins

Figure 3(a) shows the infrared spectra of the lignin samples studied (LIG-1, LIG-2, and LIG-3). The spectra show some common features but also vibrations that were specific to each lignin. In the following paragraph we will analyse the recorded spectra of lignin samples on the basis of the assignments suggested by Faix (1992).

All lignins showed a broad band within the range 3410 to 3460 cm^{-1} , which is attributed to the hydroxyl groups in phenolic and aliphatic structures, and the bands around 2935 and 2848 cm^{-1} , arising from CH stretching in the aromatic methoxyl groups and the methyl and methylene groups of the side chains. A strong band of carbonyl groups was present at 1720 cm^{-1} in LIG-2 and absent in LIG1 and LIG-3. In contrast, the absorbance of the band of carbonyl groups conjugated with an aromatic ring was detected at 1648 cm^{-1} in LIG-1 and LIG-3. The absorbance of the C-H vibration of the aromatic ring at 1615 cm^{-1} and 1514 cm^{-1} , and two other bands attributed to methoxyl groups appeared at 1459 cm^{-1} and 1425 cm^{-1} . These bands are common to all lignins, although their intensities may differ.

It is more difficult to make a detailed analysis of the spectral region below 1400 cm^{-1} , since most bands are complex and have contributions from various vibrational modes. However, this region contains vibrations that are specific to the various monolignol units and enables the lignins to be structurally characterized. It is well known that in softwoods the lignin network is mainly composed of G moieties with a low content of S and only traces of p-H type units (Boeriu et al. 2004; Tejado et al. 2007). Hardwoods and dicotyl crops present different G/S ratios (Dence 1992). These differences in structure are visible in the three lignins studied. The spectrum of lignin sample LIG-1 shows the vibrations characteristic of the guaiacyl unit (1269 cm^{-1} , G ring and C=O stretch; 1140 cm^{-1} , CH in-plane deformation; 854 cm^{-1} and 817 cm^{-1} , C-H out-of-plane vibrations in position 2, 5 and 6 of the guaiacyl units) which is characteristics of softwood lignins. The spectra of non-wood lignins from rice and wheat, respectively, LIG-2 and LIG-3, show one band at 1326 cm^{-1} that is characteristic of the syringyl (S) ring plus guaiacyl (G) ring condensed; another at 1115 cm^{-1} that is characteristic of aromatic C-H in S units; and a vibration at 843 cm^{-1} that arises from the C-H out-of-plane vibration at position 2 and 6 of the S units. The first two bands are more intense in LIG-2 than in LIG-3, and the third band is weak in LIG-2 and LIG-3.

Common to the spectra of all lignin samples, there was a weak band at 1370-1375 cm^{-1} corresponding to phenolic OH and aliphatic C-H in the methyl groups; a strong vibration in LIG1 and LIG-2; and a weak vibration in LIG-3 at 1215-1220 cm^{-1} that can be attributed to C-C plus C-O plus C=O stretching. The ether-O- at 1043 cm^{-1} was very intense in LIG-1, intense in LIG-3, and weak in LIG-2.

As a resin component, lignin can react with formaldehyde and phenol by heating under alkaline conditions to produce resol. In the first step of the reaction, hydroxymethyl groups are introduced into the lignin's reactive positions, mainly into ortho-positions in relation to the OH groups of the aromatic rings (see Fig. 1). In lignin, G and p-H-type units have free C-3 and C-5 positions in the phenolic ring which are reactive with formaldehyde, while in the S-type units both the C-3 and C-5 positions are blocked by

methoxyl groups. From this criterion, the LIG-1 with most G-type units appeared to be the best of all the lignin samples studied for producing phenolic resins, especially the phenol formaldehyde resole type.

Proton NMR Spectroscopy of Acetylated Lignins

From the spectrum of acetylated lignin sample LIG-2 presented in Fig. 3 it can be seen that the integration of proton signals into the ^1H NMR spectrum is hampered by overlapping signals. Even so, by comparison with the signal for methoxyl protons the number of protons for each functional group can be estimated. The ^1H -NMR signals of acetylated pine lignins, as indicated by Lundquist et al. (1980), are listed in Table 1. Table 2 lists the ratios of acetate groups to methoxyl groups in lignin samples after acetylation, as estimated from the ratios between the signals, together with the estimated total of the aliphatic and aromatic acetate signals. It also lists the content of phenolic hydroxyl groups as estimated by UV-spectroscopy method.

From the results of Table 2 it can be shown that both the alkaline lignins from rice and wheat straws (LIG-2 and LIG-3) had higher content of aliphatic and phenolic groups than those of Kraft lignin. This can be due to the method, raw material, and experimental conditions used in the pulping process.

Using sodium hydroxide extensively degrades the bonds between lignin and carbohydrates, which makes it easier to dissolve lignin in the pulping liquor with less degradation and oxidation of lignin molecules (Nada et al. 1998). This can also be due to the greater hydrolysis of the methoxy groups and the ether linkages between the lignin polymers in LIG-2 and LIG-3. The lower content of hydroxyl groups in kraft lignin (LIG-1) can be attributed to the repolymerization process of the lignin fragments during the kraft pulping when a highly severe treatment is applied.

Although kraft lignin contains relatively less phenolic and hydroxyl groups than the other two lignins analysed, the fact that it comes from G-type units means that there are more unsubstituted 3- or 5-positions on the phenolic ring of the lignin molecule, which suggests that it could be used for the polymerization reaction in the phenol formaldehyde resin. To prepare epoxy lignin resin the epichlorohydrin reacts with the hydroxyl groups to form epoxy groups. Therefore, LIG-2 and LIG-3, from rice and wheat straws, respectively, with higher hydroxyl groups content could be a good raw material for lignin-based epoxy resins.

Molecular Weight Distribution

The molecular weight distributions of acetylated lignin samples were obtained by size exclusion chromatography (SEC). Acetylation was carried out in order to fully dissolve the lignin sample in the chromatographic eluent (tetrahydrofuran). Figure 5 shows the corresponding molecular weight distributions of the acetylated lignins. The molecular weights are relative, because PS calibration was used. It can be seen that the shape of the MWD curves of all the lignins were the same and that the curves were normal.

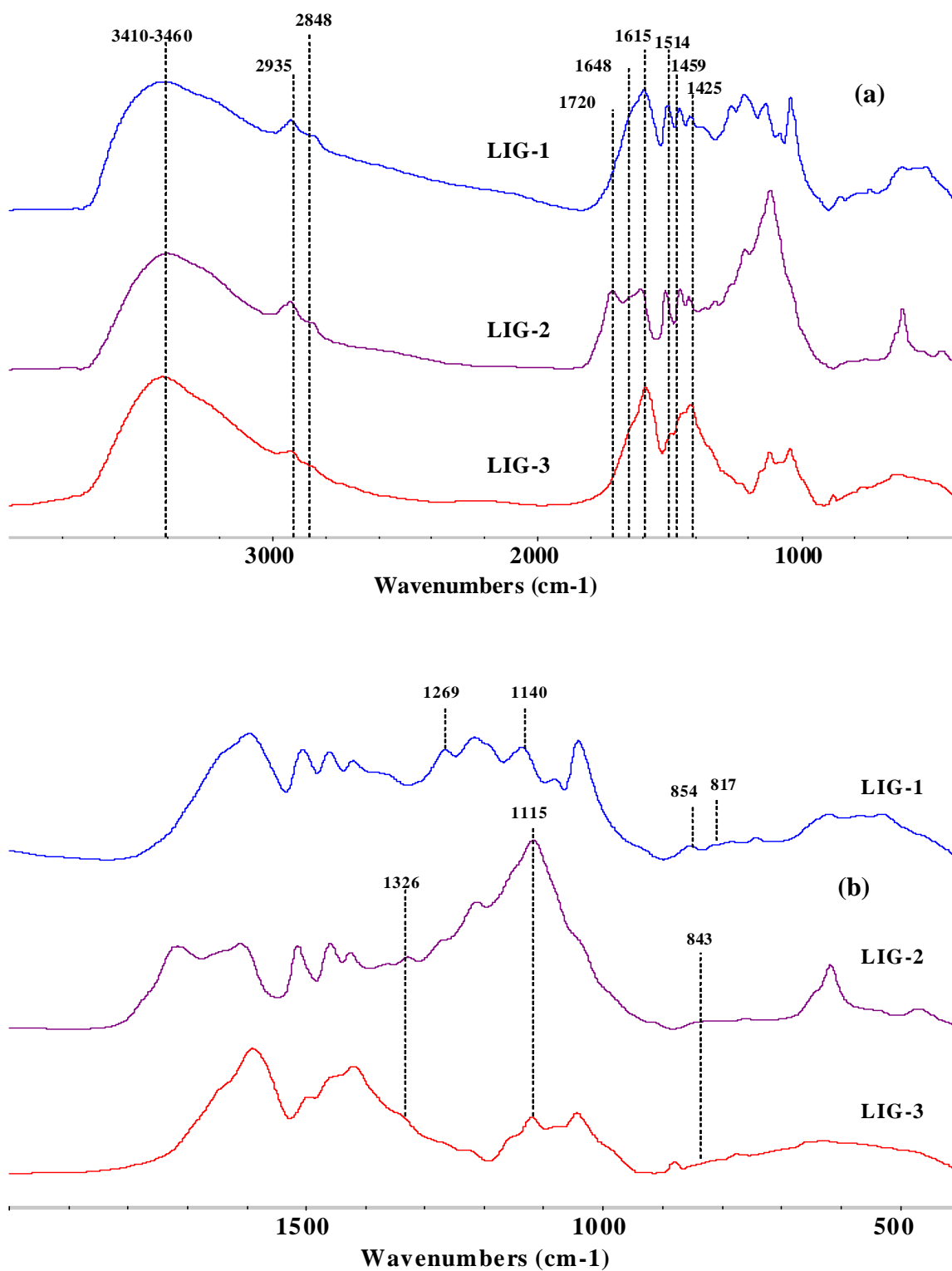


Fig. 3. FTIR spectra of (a) LIG-1, LIG-2, and LIG-3 lignin samples, and (b) detail of the 2000-400 cm⁻¹ range

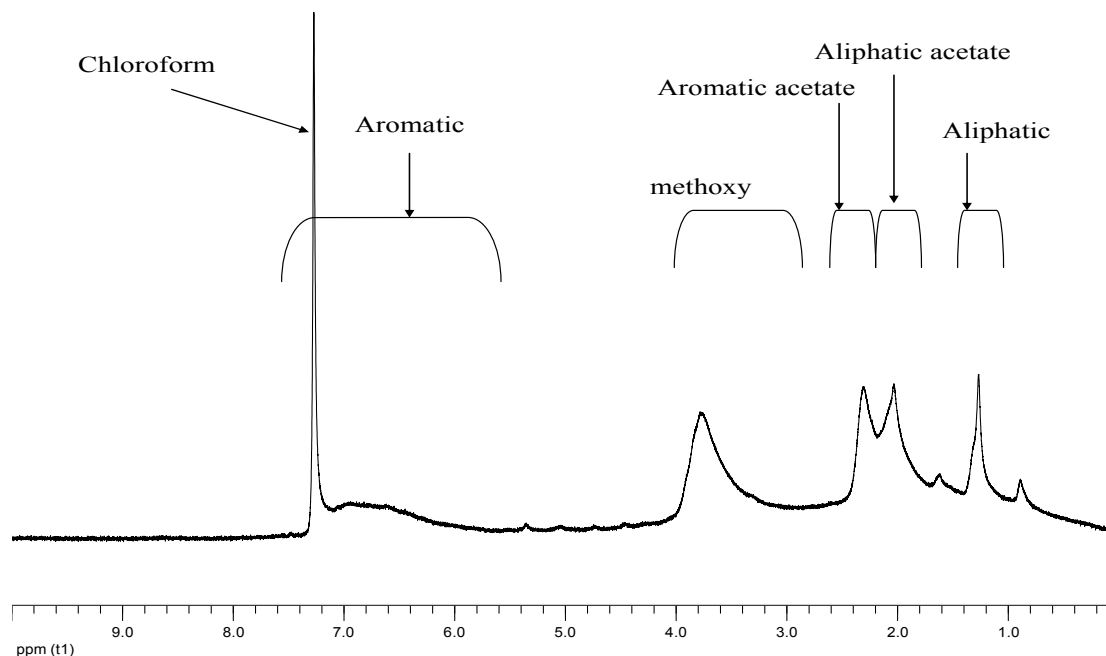


Fig. 4. $^1\text{H-NMR}$ spectrum of acetylated soda-rice straw lignin (LIG-2)

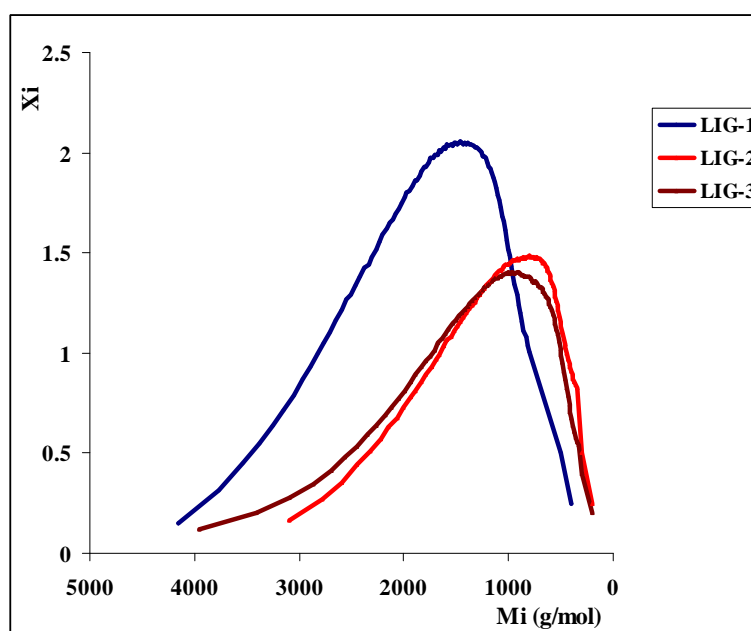
Table 1. $^1\text{H-NMR}$ Signals of Acetylated Pine Lignins and Structural Assignments

δ^b , ppm	Assignment
2.04	Aliphatic acetate
2.31	Aromatic acetate
2.58	Benzylic protons in β - β structures of secoisolariciresinol type, benzylic protons in 3-aryl-1-propanol units
3.82	Protons in methoxyl groups
4.21	H γ in several structures
4.70	H α in β - β structures
5.34	H α in β -5 structures (H α in noncyclic benzyl aryl ethers, H β in 2-aryloxypropiofenones)
5.96	H α in β -O-4 structures (H α in β -1 structures; H β in cinnamyl alcohol units)
6.62	Aromatic protons
6.91	Aromatic protons
7.26	Chloroform (solvent)
7.42	Aromatic protons in benzaldehyde units

Table 2. Results of Numbers of Acetate groups per Methoxyl Group and Phenolic Hydroxyl Content

Samples		Kraft lignin (LIG-1)	Soda-rice lignin (LIG-2)	Soda-wheat lignin (LIG-3)
UV-spectroscopy	Phenolic hydroxyl content (%)	3.1	4.5	4.3
	Aliphatic hydroxyl content (%) ^a	4.90	6.9	6.8
¹ H-NMR spectroscopy	CH ₃ O-(4.0-3.0ppm)	1	1	1
	Aromatic-acetate (2.6-2.2 ppm)	0.50	0.75	0.70
	Aliphatic-acetate (2.2-1.6 ppm)	0.79	1.16	1.12
	Aliphatic/Aromatic	1.58	1.54	1.6
	Total (Ar+Aliph) acetates	1.29	1.91	1.82

^a: the content of aliphatic hydroxyl groups were calculated based on the ratio of aliphatic / aromatic signals from ¹H-NMR spectroscopy analysis.

**Fig. 5.** Apparent molecular weight distribution of the acetylated lignin samples

Previous studies have reported that alkaline lignins, especially kraft and soda/anthraquinone lignins, show normal curves but with a small fraction of low molecular weight oligomers (El Mansouri et al. 2006). Other lignins such as organosolv and ethanol process lignins have presented a bimodal curve, which shows that there are two lignin fractions in different amounts and with different molecular weights (El Mansouri et al. 2006).

The weight-average (M_w) and number-average (M_n) molecular weights, and the polydispersity (M_w/M_n) of the three lignin samples are shown in Table 3. The results obtained for all lignin samples are in good agreement with those presented in the literature (Angles et al. 2003; El Mansouri et al. 2006; Tejado et al. 2007; Glasser and Jain 1993). The alkaline lignin samples, LIG-2 and LIG-3, exhibited lower weight average M_w and number average M_n molecular weight than kraft lignin, LIG-1. This trend corroborates the higher phenolic hydroxyl content in these two alkaline lignins.

This is due essentially to the cleavage of α - and β -O-4 bonds, which is the predominant process during the processing of lignocellulosic materials in alkaline medium. It should also be pointed out that the polydispersity of all lignin samples is relatively low, which indicates that all lignin samples have a high fraction of their determined molecular weight.

Table 3. Results of M_w , M_n , and the Polydispersity of Acetylated Lignins

Samples	M_w (g/mol)	M_n (g/mol)	M_w/M_n
Kraft lignin (LIG-1)	1746	1501	1.16
Soda-rice lignin (LIG-2)	1069	805	1.32
Soda-wheat lignin (LIG-3)	1172	678	1.39

The difference in molecular weight can also be explained by the difference in lignin structures. In addition to ether linkages (α -O-4, β -O-4, 4-O-5), lignin also contains significant quantities of carbon-carbon linkages between the phenylpropane units. The most abundant C-C bonds in lignin molecules are those with a C5 position in the aromatic ring. G-type units can form this type of bond, but S-type units cannot, because the C5 position is substituted by a methoxyl group (Brunow et al. 1999; Tejado et al. 2007). The C-C bonds in G-type units are not broken during wood pulping because of their high stability. As a consequence, lignins with more G-type units are expected to show higher MW than those with more S-units. This analysis seems to be valid for our samples, as their MW depends on their origin. On the other hand, the higher molecular weight of the kraft lignin (LIG-1) can also be explained by the possible repolymerization reactions occurring during the kraft pulping of lignocellulosic materials. Repolymerization increases the molecular weight of lignin. It has been reported that during kraft pulping and under highly alkaline conditions some α -hydroxyl groups form quinone methide intermediates that react easily with other lignin fragments to give alkali-stable methylene linkages (Van der Klashorst et al. 1989) and consequently cause higher molecular weight molecules to appear.

Although most research work on the use of lignin in phenolic resins supports the use of high molecular fractions of lignin (Forss and Fuhrmann 1979; Lange et al. 1983; Olivares et al. 1988; Van der Klashorst et al. 1989), it should be pointed out that lignins with high fractions of low molecular weight molecules are also suitable for condensates with phenol formaldehyde, because they are more reactive than those with high molecular weight molecules (Pizzi 1994). Because the molecular weights found in our lignin samples were relatively comparable, the G-origin and moderate hydroxyl groups of LIG-1 suggest that it is a good raw material for lignin derivatives such as lignin-based phenol-formaldehyde resins. There is no evidence to suggest that molecular weight has any influence on the properties of synthesized lignin-based epoxy resins. At this stage of characterization, we again suggest that LIG-2 and LIG-3 can be used for epoxy resin preparation.

Differential Scanning Calorimetry (DSC)

It is difficult to reliably determine the glass transition temperatures (T_g) of lignins because they are affected by molecular weight, thermal history, cross-linking, pressure, and the presence of low molecular weight contaminants, including water and solvents (Hatakeyama 1992). Therefore, a typical T_g value for a particular lignin cannot be reported precisely. However, the differential scanning calorimetry (DSC) technique was used to determine T_g after the samples had been extensively dried at 60 °C for one day under vacuum so that the entire moisture content was released, and a relative comparison could be made between various lignin samples prepared under the same conditions.

Table 4 lists the T_g values of the lignin samples studied. The T_g values for all lignin samples were in the range 150 °C to 165 °C. They were in good agreement with those reported for different lignins with T_g values between 90 and 180 °C (Feldman et al. 2001; Glasser and Jain 1993; Tejado et al. 1997). According to Glasser and Jain (1993), T_g values are usually higher in softwood kraft lignins and lower in organosolv lignins. In our case T_g values were highest for kraft lignin (LIG1) rich in G-type units, medium for LIG-2, and lowest for LIG-3.

Table 4. Results of Thermal Analyses (DSC and TGA): T_g , DTG_{max} , and Residue Values (%)

Samples	T_g (°C)	DTG_{max} (°C)	Residue at 600 °C, (%)	Residue at 800 °C, (%)
LIG-1	165	319	56.3	46.3
LIG-2	155	410	56.3	40.4
LIG-3	150	285	56.3	40.0

T_g : glass transition temperature, DTG_{max} : maximum thermal decomposition temperature, residue (%): unvolatilized weight fraction at 600°C and 800°C

Thermogravimetric Analysis (TGA)

Thermogravimetry measures the weight change of a sample as a function of temperature or time under helium or nitrogen atmosphere. TG curves reveal the mass loss of the polymeric materials vs. the temperature of thermal degradation, and its first derivative thermogravimetry (DGT) indicates the corresponding rate of mass loss. Figure 6 (a,b) shows TG and DTG curves of several lignin samples.

The three phase changes corresponding to moisture evaporation, main devolatilization, and continuous devolatilization were comparable to the pyrolysis of biomass reported by Chen et al. (2003) and lignin reported by Murugan et al. (2008). The initial weight loss of LIG-1 and LIG-2 started at 40 °C to 50 °C and reached a maximum at 70°C to 83°C, and the offset temperature was around 110°C to 120°C, for LIG-1 and LIG-2, respectively. This change is due to the loss of water contained in the lignin polymer.

The thermal degradation step began at 185°C, 195°C, and 220°C for LIG-1, LIG-2, and LIG-3, respectively. After these temperatures the weight loss became evident. The peak of the DTG curves (DGT_{max}) can be expressed as a single thermal decomposition temperature and used to compare the thermal characteristics of polymeric materials. The thermal characteristics of the three lignin samples are given in Table 4.

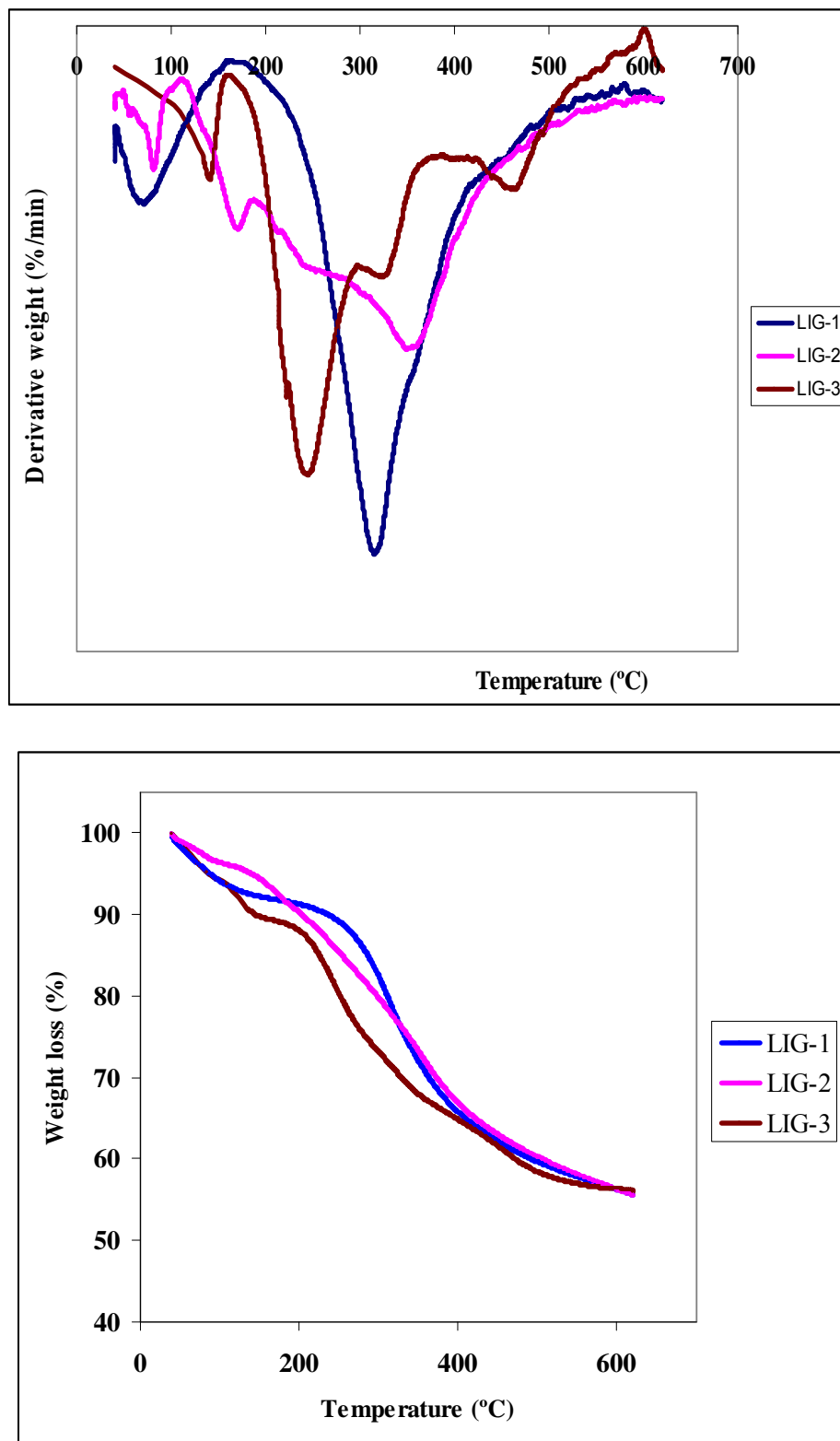


Fig. 6. (a) DTG and (b) TG curves of LIG-1, LIG2, and LIG-3

The lowest value of DGT_{max} for all lignin samples was obtained for LIG-3, while the highest value is obtained for LIG-2. In contrast, the loss of mass at 800°C was much greater for LIG-2 and LIG-3 than LIG-1. When lignin is heated to temperatures between 300°C and 450°C, pyrolytic degradation occurs and the interunit linkages fragment and release monomeric phenols into the vapor phase, while above 500°C some aromatic rings decompose (El-Saied and Nada 1993; Sun et al. 2000; Tejado et al. 2007). The range of DGT_{max} obtained is in agreement with other findings in the literature (El-Saied and Nada 1993; Sun et al. 2000; Tejado et al. 2007).

On the other hand, the maximum rate loss in phenolic resins occurred at around 345°C. Therefore, blending lignins with phenol formaldehyde resins, especially LIG-1 and LIG-2 which are more thermally stable, will lead to higher thermal decomposition temperatures. This enhanced thermal behavior may provide a wider temperature range of application for lignin-PF blends. Of the lignins LIG-2 and LIG-3, which are structurally suitable for lignin-based epoxy resins, LIG-2 had the highest thermal decomposition temperature and will therefore be selected for this purpose.

CONCLUSIONS

1. Three alkaline lignins were structurally and thermally characterized. The results were related to their origin and extraction methods, and then discussed from the point of view of their use in phenol formaldehyde and epoxy resins.
2. FTIR spectroscopy revealed that kraft lignin has more G-type units, while soda-rice straw lignin (LIG-2) and soda-wheat straw lignin (LIG-3) have more S-type units. $^1\text{H-NMR}$ spectroscopy suggests that LIG-2 and LIG-3 have more phenolic and aliphatic hydroxyl groups than kraft lignin (LIG-1). Kraft lignin (LIG-1) has higher MW than LIG-2 and LIG-3. The weight loss temperature was maximum for LIG-2, medium for LIG-1, and low for LIG-3. The glass transition temperature of all the lignins studied was between 150°C and 165°C.
3. Although kraft lignin contains less phenolic and hydroxyl groups than the other two analyzed lignins, it is recommended to be used in phenol formaldehyde resin synthesis, because it is rich in G-type units, its molecular weight is suitable, and its thermal stability is good, while LIG-2 lignin is recommended to be used in epoxy resin preparation because it has a high content of hydroxyl groups and excellent thermal stability.

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