

Physico-chemical characterization of lignins from different sources for use in phenol–formaldehyde resin synthesis

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Received 27 March 2006; received in revised form 23 May 2006; accepted 25 May 2006

Available online 14 July 2006

Abstract

During the last decades lignin has been investigated as a promising natural alternative to petrochemicals in phenol–formaldehyde (PF) resin production, due to their structural similarity. Physico-chemical characterization of three types of lignin, namely kraft pine lignin (L1), soda–anthraquinone flax lignin (L2), and ethanol–water wild tamarind lignin (L3) has been evaluated to determine which one is the most suitable chemical structure for above purpose. Characterization has been performed using Fourier transform infrared spectroscopy (FT-IR) and proton nuclear magnetic resonance spectrometry (¹H NMR) to analyse the chemical structure, gel permeation chromatography (GPC) for determining molecular weight (MW) and molecular weight distribution (MWD), differential scanning calorimetry (DSC) to measure the glass transition temperature and thermogravimetric analysis (TGA) to follow the thermal degradation. Both structural and thermal characteristics suggest that kraft pine lignin (L1) would be a better phenol (P) substitute in the synthesis of lignin–phenol–formaldehyde (LPF) resins, as it presents higher amounts of activated free ring positions, higher MW and higher thermal decomposition temperature.

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Keywords: Lignin; Characterization; Organosolv; Kraft; Soda; LPF resins

1. Introduction

With the exception of cellulose there is not a more abundant renewable natural resource than lignin, a polyphenolic macromolecule present in the cell wall of plants. Lignin is created by enzymatic polymerisation of three monomers, called coniferyl alcohol, synapyl alcohol and *p*-coumaryl alcohol that lead, respectively, to guaiacyl (G), syringyl (S) and *p*-hydroxyphenyl propane (*p*-H)-type units (Fig. 1a). The resulting structure is a complex macromolecule (Fig. 1b) with a great variety of functional groups and over 10 different types of linkages (Abreu et al., 1999; Brunow et al., 1999; Tsujino et al., 2003; Ralph et al., 1998).

Depending on the original source and extraction method used the physico-chemical characteristics of the different lignins, and thus their suitability to be used in polymer formulations, can vary noticeably.

Traditionally, lignosulfonates (lignins resulting from the sulfite pulping process) have been the only type of lignin extensively used in the industry. The polymeric character and the high content in sulfonic acid groups give them surface-active and binding properties (Rodríguez et al., 1990; Van der Klashorst, 1989). These properties have been used in several applications developed for lignosulfonates, such as dispersants (Gosselink et al., 2005; Northey, 1992) (about 90% of commercialized lignin is used as concrete additive due to this property), emulsifiers (García et al., 1984) and ion-exchange resins (Dizhbite et al., 1999; Zoumpoulakis and Simitzis, 2001). On the other hand kraft lignin, which accounts near the 85% of total lignin

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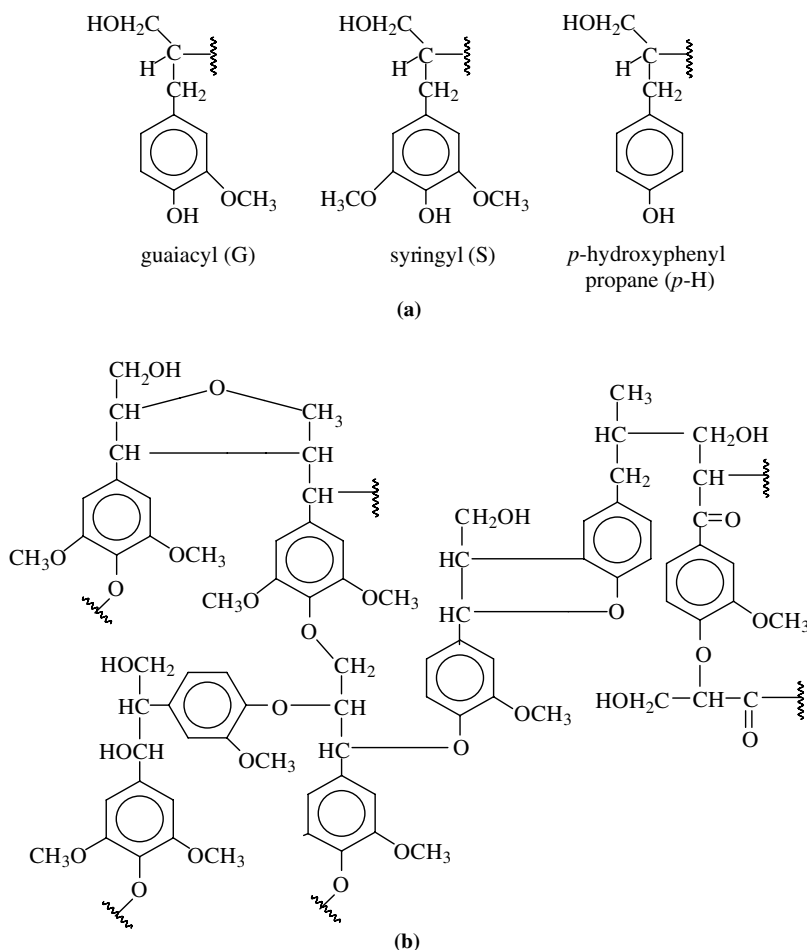


Fig. 1. (a) Schematic representation of the structural units of lignin, and (b) lignin structure proposed by Adler (1977).

production in the world, is mainly used as fuel to recover part of the energy of the pulping process. Apart from that, lignin is the raw material to obtain low molecular weight compounds like vanillin (Northey, 1992), widely used in cosmetics, simple and hydroxylated aromatics, quinones, aldehydes, aliphatic acids, etc. for which the economic feasibility is being studied (Johnson et al., 2005).

The use of lignin for the synthesis of new polymeric materials is the most promising alternative for its revalorization. In the last 20 years huge research activity has been done though industrial applications are at the moment rather scarce. Blends of lignin with thermoplastic polymers like polypropylene have shown good thermal and mechanical properties (Cazacu et al., 2004; Gosselink et al., 2004; Kadla et al., 2002). It is also being studied as compatibilizing agent between thermoplastics and natural fibers (Rozman et al., 2000, 2001). The most research activities are focused on the use of lignin as substitute of phenol in the synthesis of lignin-modified phenol-formaldehyde (LFP) resins (Alonso et al., 2004; Benar et al., 1999; Danielson and Simonson, 1998; Kazayawoko et al., 1992; Khan et al., 2004; Kharade and Kale, 1998; Peng and Riedl, 1994; Sarkar and Adhikari, 2001; Simitzis et al., 1995; Turunen et al., 2003; Vázquez et al., 1995; Ysbrandy et al.,

1997), due to the structural similarity between them. The final resin behaviour is very dependent on the chemical and physical properties of the lignin, and thus a complete characterization of it prior to the synthesis becomes of great interest.

In this work three types of lignin, namely kraft pine (*pinus radiata*) lignin, soda/anthraquinone flax (*linum usitatissimum*) lignin and ethanol/water wild tamarind (*leucaena leucocephala*) lignin have been characterized for further use in novolac-type PF resin synthesis. These lignins were extracted from black liquors kindly supplied by Smurfit Nervi3n (L1), Celulosa de Levante (L2) and the University of C3rdoba (Spain) (L3). Pine and flax are two well-known species belonging to pinaceae (softwood) and linaceae (dicotyl crop) families, respectively. Wild tamarind belongs to the leguminosae family (hardwood) and is one of the fastest-growing leguminous trees. It is an important species encouraged under the social forestry schemes in drought-prone areas and semi-arid tracts.

2. Experimental

Lignins from kraft and soda/anthraquinone liquors (L1 and L2), commonly named alkali lignins, were extracted by

acid precipitation. According to Sharma and Goldstein (1990), HCl-isolated lignin samples show higher reactivity towards phenol than those isolated using sulfuric acid, for this reason we have used a solution of 1 M hydrochloric acid. After lowering the pH to 2 the precipitated lignins were filtered on a Buchner funnel and successively washed with water twice, to remove unreacted compounds and degraded sugars, and then dried in an oven at 60 °C under vacuum.

Isolation of organosolv (ethanol/water) lignin (L3) was performed under a liquor-to-water ratio of 1:2 and acidulation with HCl to pH 2. Such conditions are reported to be adequate for extraction (Botello et al., 1999; Vila et al., 2003). The lignin sample obtained after centrifugation at 3500 rpm for 10 min was washed twice and dried in an oven at 60 °C under vacuum until constant weight was obtained.

Lignin samples were subjected to acetylation in order to enhance their solubility in organic solvents, used in both GPC and NMR techniques. This reaction implies the substitution of all the hydroxylic functions by new acetyl groups. With that purpose, the three lignins were placed in an acetyl anhydride/acetyl acid mixture (1:1 by weight) containing sodium acetate as a catalyst (0.5 equivalents per mole of acetyl anhydride), being the final lignin concentration 20 wt% (Glasser and Jain, 1993). Reactions were carried out at room temperature for 48 h and then refluxed for 1 h. Products obtained by precipitation in ice-cold water with 1% HCl were filtered, washed with distilled water and dried in the same way as the isolated lignin samples.

FT-IR measurements were performed in a Perkin–Elmer 16PC instrument by direct transmittance using KBr pellet technique. Each spectrum was recorded over 20 scans, in the range from 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1} . Background spectra were collected before every sampling. KBr was previously oven-dried to avoid interferences due to the presence of water. The chemical structure of samples has also been studied through ^1H NMR spectrometry using a Bruker 500 MHz spectrometer at a frequency of 250 MHz with an acquisition time of 0.011 s. DMSO has been used as solvent.

Gel permeation chromatography provides a rapid way to obtain information on the molecular weight of polymers. Samples have been examined through THF-eluted GPC using a Perkin–Elmer instrument equipped with an interface (PE Series 900). Three Waters Styragel columns (HR 1, HR 2 and HR 3) ranging from 100 to 5×10^5 and a refractive index detector (Series 200) were employed, with a flow rate of 1 mL/min. The calibration was made using polystyrene standards.

Glass transition temperatures (T_g) were determined using a Mettler DSC20 differential scanning calorimeter linked to a TC 15 TA processor by using medium pressure pans. The scans were run at 10 °C/min under a nitrogen flow rate of 10 mL/min. Before being tested, the samples were extensively dried for 24 h in an oven at 60 °C under

vacuum to eliminate the presence of water. The T_g was defined as the mid point of the temperature range at which the change in heat capacity occurs. The thermal stability of lignin was measured using a TGA-92 thermobalance from Setaram under dynamic scans from 30 to 800 °C at 10 °C/min with helium atmosphere.

3. Results and discussion

3.1. Chemical structure

3.1.1. FT-IR spectroscopy

The FT-IR spectrum (Fig. 2a) of all lignin samples show bands at 1600, 1515 and 1425 cm^{-1} corresponding to aromatic ring vibrations of the phenylpropane skeleton. A wide absorption band focused at 3400 cm^{-1} is assigned to aromatic and aliphatic OH groups while bands at 2960, 2925, 2850 and 1460 cm^{-1} are related to the C–H vibration of CH_2 and CH_3 groups. Bands assignment is shown in Table 1.

Some remarkable singularities due to their different origin can be observed. It is well known that in softwoods the lignin network is mainly composed by G moieties with small contents of S and only traces of *p*-H type units (Boeriu et al., 2004) while in hardwoods and dicotyl crops different amounts of G/S have been reported (Dence, 1992). These characteristics become visible in the spectra of the three studied lignins. L1 presents mainly G bands (1270, 1125, 855 and 810 cm^{-1}), while L2 shows typical S bands (1326, 1115 and 825 cm^{-1}) as it was expected. L3, coming from the fast-growing hardwood specie, clearly shows a mixture of both types of units, as remarked in Fig. 2b.

Bands in the range of 1705–1715 cm^{-1} shown by L1 and L3 can be attributed to non-conjugated carbonyl groups and the wideness of the 1600 cm^{-1} band in L2 spectrum can be related to the presence of conjugated carbonyl groups (focused at 1650 cm^{-1}) in its structure.

The delignification method used for the isolation of lignin plays an important role in the final structure (Fig. 3). Kraft method cleaves β -O-4 and α -O-4 linkages leaving a lot of non-etherified phenolic OH groups in lignin, visible in L1 spectrum at 1365 cm^{-1} . On the other hand, soda pulping of non-woody materials produces the cleavage of those aryl-ether linkages through the formation of small quantities of phenolic hydroxyls (Gellerstedt and Lindfors, 1984) and the loss of primary aliphatic OH. This can also be seen in L2 spectrum, where there is practically no vibration at 1365 cm^{-1} and the signal of 1030 cm^{-1} , attributed to primary OH (among others), is less intense than in the other samples. In the organosolv method (L3) that uses an ethanol/water mixture as pulping solvent the acetic acid released from the hemicelluloses of wood is the chemical agent that leads to lignin dissolution. This method promotes the acid hydrolysis of lignin generating both phenolic hydroxyl groups (visible at 1365 cm^{-1}) and new carbonyl groups (1715 cm^{-1}) in its structure.

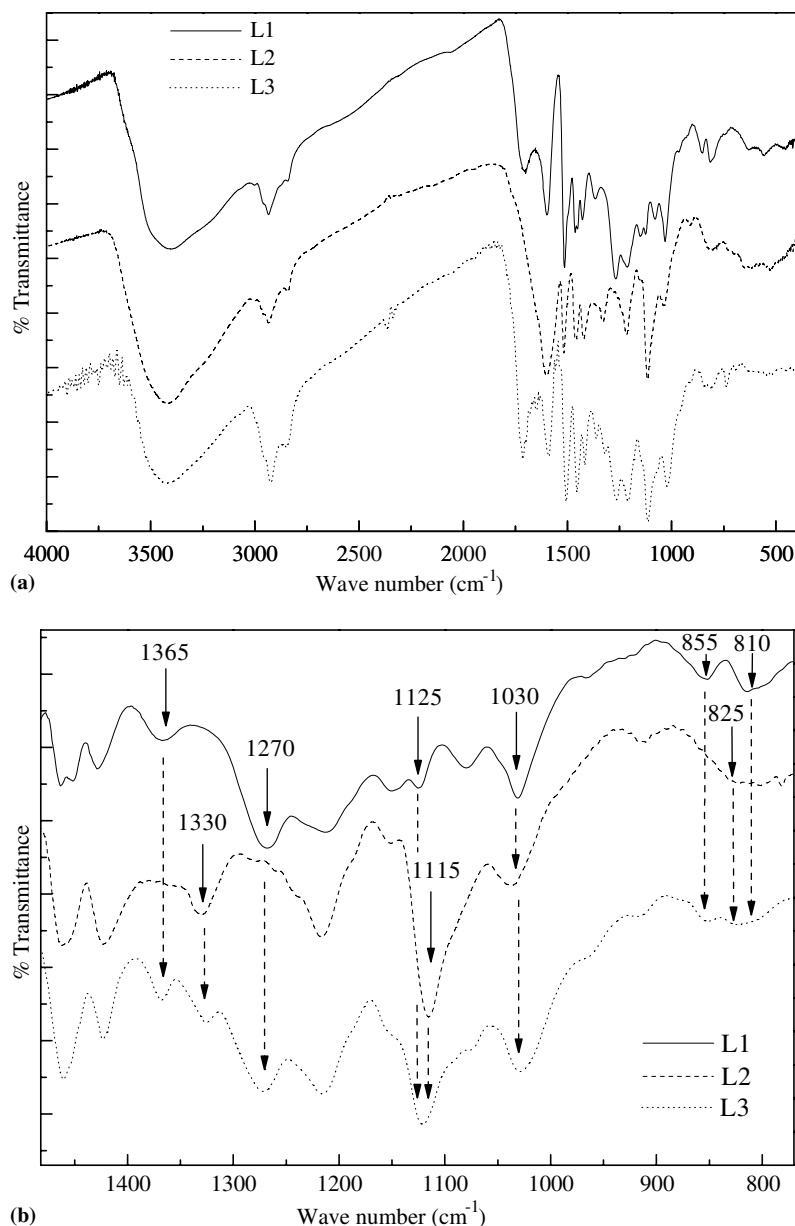


Fig. 2. (a) FT-IR spectra of L1 (—), L2 (--) and L3 (···) samples, and (b) detail of the 1480–770 cm⁻¹ range.

Polymerisation reactions during the synthesis of PF resins take place through electrophilic substitution of F at a free position of the aromatic ring. In lignin, G-type units have a free C5 position (*ortho* to the phenolic hydroxyl) in the ring, susceptible of reacting with F, while in S-type units both C3 and C5 positions are linked to a methoxy group, resulting in low reactivity with F. From this point of view, lignins with G groups as the principal structural units must be *a priori* more suitable for PF formulations. Another factor that must be considered is the existence of big quantities of phenolic hydroxyls in the lignin structure: they activate the free ring positions making them reactive with F, but they can also promote higher non-covalent interactions between lignin moieties making lignin behave as a crowded and stiff macromolecule (Feldman et al.,

2001; Thring et al., 2004). In lignin–phenol–formaldehyde (LPF) formulations this fact can cause an important decrease of final properties (Kazayawoko et al., 1992; Kharade and Kale, 1998; Peng and Riedl, 1994; Sarkar and Adhikari, 2001; Vázquez et al., 1995; Ysbrandy et al., 1997).

3.1.2. ¹H NMR spectrometry

The chemical structure of acetylated lignin samples has been studied through ¹H NMR spectrometry. Fig. 4 shows the ¹H NMR spectra of acetylated lignin samples (AL1, AL2 and AL3). As pointed out in Table 2, the integral of all signals between 6.0 and 8.0 ppm can be attributed to aromatic protons in S and G units, while those between 0.8 and 1.5 ppm are related to the aliphatic moiety in the

Table 1
FT-IR bands assignment

Band (cm ⁻¹)	Vibration	Assignment
3420–3405	st O–H	Phenolic OH + aliphatic OH
2960–2925	st C–H	CH ₃ + CH ₂
2850–2840	st C–H	OCH ₃
1705–1715	st C=O	Unconjugated C=O
1650	st C=O	Conjugated C=O
1600	st C–C	Aromatic skeleton
1515	st C–C	Aromatic skeleton
1460	$\delta_{\text{asymmetric}}$ C–H	CH ₃ + CH ₂
1425	st C–C	Aromatic skeleton
1365	δ_{ip} O–H	Phenolic OH
1326	st C–O	S
1270	st C–O	G
1220	st C–O(H) + C–O(Ar)	Phenolic OH + ether
1125	δ_{ip} Ar C–H	G
1115	δ_{ip} Ar C–H	S
1030	st C–O(H) + C–O(C)	1st order aliphatic OH + ether
855	δ_{op} Ar C–H	G
825	δ_{op} Ar C–H	S
810	δ_{op} Ar C–H	G

st: Stretching vibration.

δ_{ip} : In-plane deformation vibration.

δ_{op} : Out-of-plane deformation vibration.

lignin. Methoxyl protons (–OCH₃), closely related to G:S proportion, give an intense signal centred at 3.8 ppm.

Acetylation produces derivatives that display broad proton signals in regions with small interference with other hydrogen signals. In addition, aromatic and aliphatic acetyl groups are shifted differently (2.3 and 2.1 ppm, respectively) giving rise to separate peaks. Thus, ¹H NMR spectrometry of acetylated lignin samples reveals both the total content of acetyl groups (proportional to OH content) and the ratio between aromatic and aliphatic substituents (Glasser and Jain, 1993).

Table 3 shows the results derived from these analyses. By integration of the different signals, the following parameters can be calculated: the ratio between G and S structures (G:S), the content in aromatic protons (aromatic H), methoxyl groups (OCH₃) and total hydroxyl groups (OH_{total}) per average phenylpropane unit (C₉), and the ratio between phenolic and aliphatic hydroxyls (OH_{ph}:OH_{al}). All calculations have been made supposing that lignin samples are only composed by G and S-type units. As expected, acetylated L1 exhibits higher content of aromatic protons than L2 and L3, as the former is mainly composed by G units. Therefore, it will show *a priori* higher reactivity towards electrophilic substitution reactions. L2, with majority of S units, presents high quantities of methoxyl groups as shown by FT-IR results, while L3 shows an intermediate behaviour. Total OH content is much bigger for kraft pine lignin (L1) than for alkali flax lignin (L2) as shown by FT-IR results, being L3 in the middle of them. On the other hand, the relative quantity of aromatic and aliphatic hydroxyls is similar for all samples and can be explained by taking into account the effect of the pulping method suggested above: while kraft and organosolv pulping generate phenolic OH in L1 and L3 samples respectively, soda process eliminates aliphatic OH from L2.

3.2. Molecular weights

3.2.1. Gel permeation chromatography

The molecular weights of lignin samples have been analysed through THF-eluted GPC. As shown before lignin samples have been acetylated to enhance their solubility in such solvent. Data and chromatograms obtained for lignin preparations, shown in Table 4 and Fig. 5 respectively, are in overall agreement with published reports (Anglès

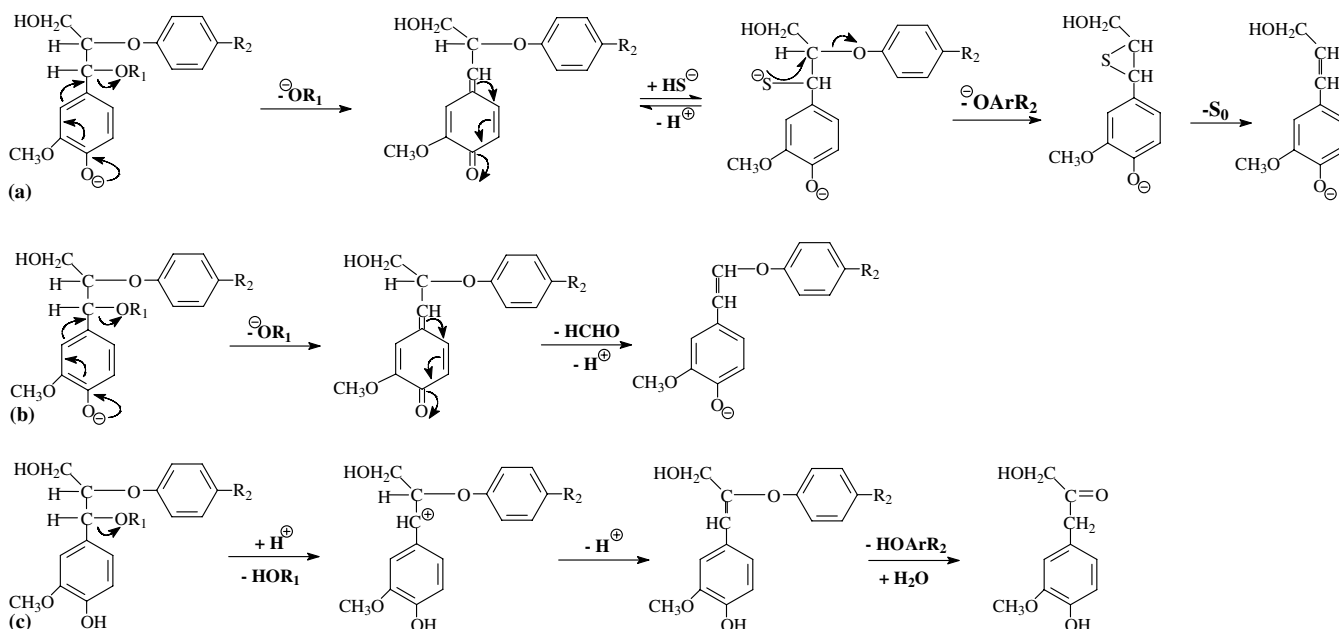


Fig. 3. Schematic representation of the main changes occurring in the lignin structure during the (a) kraft, (b) soda and (c) ethanol/water processes.

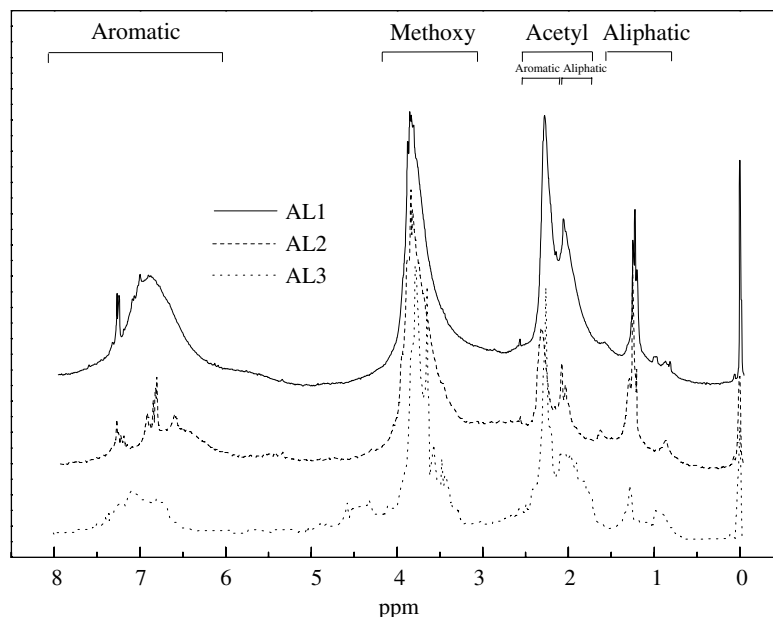


Fig. 4. ^1H NMR spectra of acetylated L1 (—), L2 (--) and L3 (···) samples.

Table 2
Signal assignment for ^1H NMR spectrometry of acetylated lignin samples

Signal (ppm)	Assignment
8.0–6.0	Aromatic H in S and G units
6.9	Aromatic H in G
6.6	Aromatic H in S
3.1–4.2	Methoxyl H
2.5–2.2	H in aromatic acetates
2.2–1.9	H in aliphatic acetates
1.5–0.8	Aliphatic H

Table 3
Chemical structure of lignin samples studied by ^1H NMR

Sample	G:S ^a	Aromatic H /C9 ^b	OCH ₃ /C9	wt% wt%	OH _{total} /C9	mmol/g	OH _{ph} :OH _{al}
L1	73:27	2.73	1.2	20.9	1.23	6.52	0.54
L2	19:81	2.19	1.8	27.5	0.82	4.01	0.54
L3	28:72	2.29	1.5	22.6	1.17	5.81	0.49

^a All calculations have been done considering MW of 180 and 210 g/mol for G-type and S-type units, respectively.

^b C9 represents one phenylpropane structural unit.

Table 4
Weight average MW ($\overline{M}_w$), number average MW ($\overline{M}_n$) and polydispersity ($\overline{M}_w/\overline{M}_n$) of acetylated lignin samples analysed by GPC

Sample	$\overline{M}_w/10^3$	$\overline{M}_n/10^3$	$\overline{M}_w/\overline{M}_n$
AL1	8.7	2.4	3.6
AL2	2.6	1.5	1.8
AL3	3.1	1.7	1.8

et al., 2003; Gellerstedt and Lindfors, 1984; Glasser and Jain, 1993).

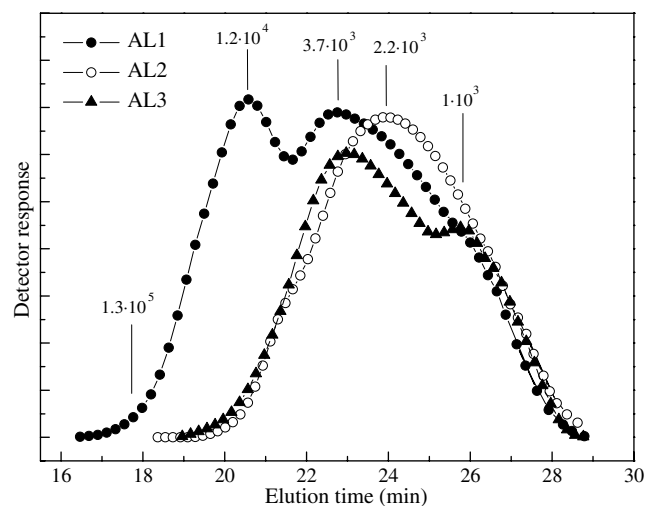


Fig. 5. GPC chromatograms of acetylated L1 (●), L2 (○) and L3 (▲) samples.

AL2 and AL3 samples show weight average MW of 2.6×10^3 and 3.1×10^3 while AL1 presents a much higher value, close to 10^4 . These results can be explained according to the different lignin composition. Although β -O-4 is the most common linkage in all lignin types, there are also important quantities of C–C bonds between the structural units; among them, those involving C5 of the aromatic ring are the most abundant (Brunow et al., 1999; Sjöholm, 1999; Sjöström, 1981). G-type units are able to form this kind of bonds, but this is not possible in S-type units as they have C5 position substituted by a methoxy group. This is a very important feature when studying the MW of lignins because these C–C bonds are not cleaved during the pulping of wood due to their higher stability. As a con-

sequence, lignins strictly composed by G units are expected to show higher MW than those presenting high contents of S units. This seems to be valid for the lignin samples studied in this work, as their MW is correlated with their G content.

Repolymerisation reactions may be promoted during alkaline pulping affecting the MW of lignins. Under highly alkaline conditions some α -hydroxyl groups form quinone methide intermediates that react easily with other lignin fragments giving alkali-stable methylene linkages (Ishizu et al., 1958; Van der Klashorst, 1989). This reaction, occurring especially during kraft method due to the more severe conditions used, causes the appearance of high MW species that lead to higher average MW and MWD values.

Most of the research works found in the literature support the utilization of high MW fractions of lignin for the synthesis of modified phenolic resins (Forss and Fuhrmann, 1979; Lange et al., 1983; Olivares et al., 1988; Van der Klashorst, 1989). Due to the larger number of phenylpropane units per fragment, each fragment has a much better chance to contribute to polymerisation, compared with the monomeric and dimeric fractions (Van der Klashorst, 1989). For this reason and due to its higher content of aromatic protons, L1 would be more appropriate for this aim than the other lignin samples.

3.3. Thermal behaviour

3.3.1. Differential scanning calorimetry

Glass transition temperature (T_g) of lignins are often too indiscernible to be determined with reliability and they are also very influenced by the water content. For this reason, T_g have been determined by DSC scans after extensively drying the samples (60 °C, 24 h, vacuum-oven dried) in order to release all the moisture content.

Different underivatized lignin preparations are reported to have T_g values between 90 and 180 °C (Feldman et al., 2001; Glasser and Jain, 1993), corresponding the higher values usually to softwood kraft lignins and the lower ones to organosolv lignins (Glasser and Jain, 1993). These ranges show good agreement with our data, as shown in Table 5.

3.3.2. Thermogravimetric analysis

The thermal decomposition of organic polymers is commonly determined by thermogravimetric (TG) analysis under helium or nitrogen atmosphere. TG curves reveal the weight loss of substances in relation to the temperature

of thermal degradation, while the first derivative of that curve (DTG) shows the corresponding rate of weight loss. The peak of this curve (DTG_{max}) may be expressed as a single thermal decomposition temperature and can be used to compare thermal stability characteristics of different materials. The DTG_{max} appears between 350 and 425 °C for all lignin samples analysed, as can be seen in Fig. 6 and Table 5. Pyrolytic degradation in this region involves fragmentation of inter-unit linkages, releasing monomeric phenols into the vapour phase, while above 500 °C the process is related to the decomposition of some aromatic rings (El-Saied and Nada, 1993; Sun et al., 2000). The DTG_{max} for non-wood lignin (L2) is clearly lower than for L1 and L3, what can be related to the above mentioned different content in C–C linkages. These data are again in agreement with those found in the literature (El-Saied and Nada, 1993; Glasser and Jain, 1993; Sun et al., 2000).

After heating to 800 °C the 40–50 wt% of all lignin samples still remains unvolatilized due to the formation of highly condensed aromatic structures. This thermal characteristic has also been reported for PF resins (Gabilondo, 2004) and remarks the similarities between both types of

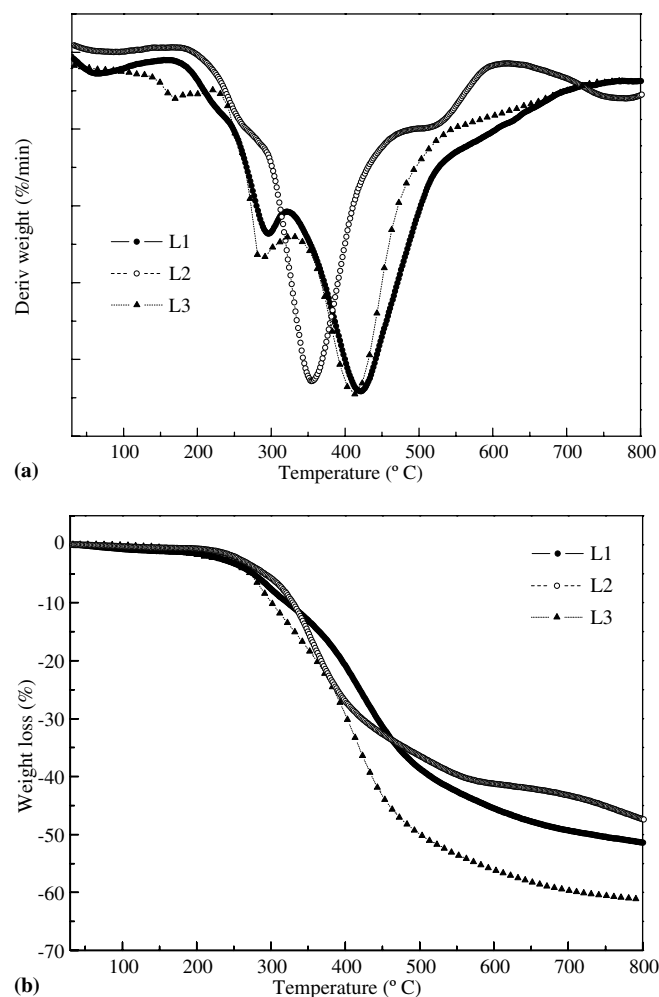


Fig. 6. (a) DTG and (b) TG curves of L1 (—●—), L2 (---○---) and L3 (---▲---) obtained from TGA analysis.

Table 5

Values of glass transition temperature (T_g), maximum of thermal decomposition temperature (DTG_{max}) and unvolatilized weight fraction at 800 °C (residue) for all lignin preparations

Sample	T_g (°C)	DTG _{max} (°C)	Residue (%)
L1	144	421	48
L2	138	356	53
L3	100	413	38

substances. The maximum rate loss in non-modified novolac resins occurs at 345 °C. Therefore the introduction of lignins in PF formulations, especially those with higher thermal stability, will lead to higher thermal decomposition temperatures. This enhanced thermal behaviour may suppose a wider temperature range of application for lignin-modified PF resins.

4. Conclusions

Physico-chemical characterization of three lignin samples has been performed, and the results have been related to their different origin and different extraction method. FT-IR spectroscopy and ¹H NMR spectrometry reveal that kraft pine lignin (L1) is mainly composed by G units with high quantities of non-etherified hydroxyl groups, while soda/AQ flax lignin (L2) shows mainly S units and less free hydroxyls; organosolv hardwood lignin (L3) presents both G and S structural units. Molecular weight of lignin samples has been studied through THF-eluted GPC showing that L1 has much higher MW and MWD than the other samples. This behaviour is related to its higher content in C–C linkages and to repolymerisation reactions occurring during kraft pulping. Finally, L1 and L3 show degradation temperatures up to 80 °C above that of unmodified novolac PF resin. Both structural and thermal characteristics analysed suggest that L1 will be *a priori* a better P substitute in the synthesis of LPF resins, as it presents higher amount of activated free ring positions, higher MW and higher thermal decomposition temperature.

Acknowledgements

The authors wish to thank Bakelite Ibérica, Gobierno Vasco/Eusko Jaurlaritza (OD02UN46) and Ministerio de Educación y Ciencia (CTQ2004-06564-C04-03/PPQ) for their financial support of this work.

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