STRUCTURE AND THERMAL PROPERTIES OF LIGNINS: CHARACTERIZATION BY INFRARED SPECTROSCOPY AND DIFFERENTIAL SCANNING CALORIMETRY

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ABSTRACT

After cellulose, lignin is, the second most abundant component in wood. In the pulping industry, the introduction of modern Kraft pulping technologies could produce chemical modification in lignin's functional groups.

Kraft lignins from *Eucalyptus nitens* and *Pinus radiata* industrial black liquors were isolated by acid precipitation. An organosolv lignin was obtained from spent liquor from the P. radiata wood pulping process.

All lignins were acetylated with acetic anhydride and characterized by Fourier-transformed infrared spectroscopy (FT-IR).

Analysis based on the IR-fingerprint spectral region indicates several differences in the functional groups of the different types of lignins.

The thermal behaviour of unmodified and acetylated lignins were studied by differential scanning calorimetry (DSC) and the glass transition temperatures (Tg) were determined and compared with values reported in the literature.

The acetylated lignins show a decrease in the Tg values which is probably due, to the at plasticization effect of the acetylation reaction.

Keywords : lignins, infrared spectroscopy, glass transition temperatures.

INTRODUCTION

Lignin is a phenolic polymer present in large amounts in plants cells and wood tissues. It is the second most abundant natural polymer after cellulose.

This macromolecule is complex and it is widely accepted that the biosynthesis of lignin stems from the polymerization of three types of phenylpropane units, also referred to as monolignols.^{1,2,3,4} These units are coniferyl, sinapyl and p-coumaryl alcohol. The three structures are depicted in Figure 1.

Fig. 1. Units of monolignols presents in lignins

The main source for technical lignins is the black liquor from the pulping process.^{5,6} In the pulping industry, vast amounts of lignin are separated from wood and then, burned internally in the pulp mill to produce steam and electricity, except for those produced for specialty chemical purposes.⁷

In terms of global industrial lignin production, the Kraft pulping process is the principal process.

Numerous studies have been conducted over the past two decades to elucidate the chemical structure of Kraft lignins using different techniques. The most important ones used are: nuclear magnetic resonance (NMR)^{8,9,10}, infrared spectroscopy (IR)^{11,12}, ultraviolet spectroscopy (UV)¹³, chemical and functional characterization^{14,15}, pyrolysis-gas chromatography¹⁶ and others.

The use of Fourier-transform infrared spectroscopy (FT-IR) to determine the functional groups in lignin is well described in the literature. Hergert¹⁷, Faix¹⁸, Schultz and Glasser¹⁹ and more recently Chipanina *et al*²⁰, described qualitatively the occurrence of carbonyl (C=O) groups, aromatic structures, C_{aliph}-O and C_{arom}-O bonds and also the substitution pattern in the benzene ring.

New delignification processes based on organic solvents or the changes introduced with the modern Kraft pulping technologies could produce

chemical modification in lignin's functional groups. These changes in the chemical structure have an important influence on lignin's physical and thermal properties.

The introduction of new higher resolution FT-IR equipments to study lignocellulosic materials^{21,22} and the utilization of non-conventional wood species such as *Eucalyptus nitens* in the Kraft pulping process have created the possibility to carry out the present study.

The aim of this work was use FT-IR to study the principal functional groups of *Pinus radiata* and *Eucalyptus nitens* lignins in Kraft black liquors in order to compare them with an organosolv lignin. Also, we report the thermal behaviour of these non-acetylated and acetylated lignins in order to study the influence of the acetylation reaction on the glass transition temperature (Tg) of lignin to utilize its as plastic antioxidants in future studies.

EXPERIMENTAL

Eucalyptus nitens and *Pinus radiata* black liquors of the Kraft pulping process were supplied by CMPC Industry (Nacimiento-Chile) and Arauco Industry (Arauco-Chile), respectively.

The organosolv lignin was obtained from the spent liquor of the P. radiata wood pulping process with a formic acid - acetone mixture. The pulping conditions were:

Wood/liquor ratio: 1g / 6mL. Formic acid / acetone : 70 / 30 v/v. Pulping time: 23 minutes. Temperature of cooking: 165°C.

The pulping was performed in the Renewable Resources Laboratory (Universidad de Concepción)²³.

The Kraft black liquors were initially filtered through a Whatman N° 4 filter paper and then the pH and solid content were determined.

The liquors were concentrated at 28-30 % solid content in a rotary evaporator at 70°C.

The liquors were then neutralized with 2 M H₂SO₄ to pH 7.0, stirred for 1 hour and then further acidified to pH 3.0. At this pH lignin precipitates and two phases are obtained. The lignin was stirred for 30 minutes and then filtered and washed several times with 1 M HCl to eliminate salts and some carbohydrates.

The isolated solid lignins were dried in a drying oven at 70°C for 12 hours.

Acetylation

The acetylation reaction of the different lignins was carried out using a method similar to the one used for wood flour.²⁴

The method is the following: 2 g dry lignin was placed in a 300 mL flat bottom flask and 100 mL of acetic anhydride was added. The flask was

dipped into an oil bath set at 120°C and fitted with a reflux condenser. Once the reaction of 1 hour was completed, the flask was removed from the oil bath and the lignin was filtered.

The acetylated lignin was oven dried at 70°C for 16 hours and then weighed.

FT-IR spectroscopy

The FT-IR analysis of unmodified and acetylated lignins were recorded on a Nicolet model Nexus spectrophotometer, using KBr pellets containing 1 % finely ground samples.

DSC analyses

The thermal analysis of unmodified and acetylated lignins was carried out by means of a METTLER TOLEDO differential scanning calorimeter (DSC 822^e) equipped with a thermal analysis data STAR^e software system.

All the results of differential scanning calorimetry represent the average of at least five determinations. Samples of about 5-10 mg were run at a heating rate of 10°C/min under nitrogen atmosphere between 30°C and 150°C to remove previous thermal history.

For Tg determinations, a heating rate of 20°C/min was used, because the glass transition is more pronounced at faster heating rates.²⁵

RESULTS AND DISCUSSION

Table 1 shows the solid content and pH of E. nitens and P. radiata industrial black liquors.

Table 1. Physical properties of industrial Kraft liquors.

Kraft liquor	Solid content (%)	pH
E. nitens	14	10.5
P. radiata	18	11.5

Table 2 describes the lignin yield, where a very similar lignin yield for E. nitens and P.radiata Kraft black liquors is observed after the precipitation and washing process. The low ash content indicates the high purity levels in the lignin obtained in the process.

Table 2 . Recuperation of Kraft lignins from industrial liquors.

Kraft lignin	Solid content (%)	Total solids acidified (g)	Total lignin mass (g)	Recuperation (%)	Ash content (%)
Kraft eucalipto	28	148	48	32.4	0.65
Kraft pino	30	242	80	33.0	0.55

FT-IR characterization of lignins

Table 3 presents the wavenumbers and the important band identifications found.

Table 3. Bands assignments of the non-acetylated lignins

Lignin	Peak wavenumber (cm ⁻¹)			
Unmodified lignin	K.pino	K.eucalipto	Organosolv	Band assignment
	3414	3423	3423	Stretching vibrations in O-H
	2935	2928	2937	CH stretching vibrations
	-	2851	-	Tertiary CH groups
	1714	1715	1712	Unconjugated carbonyls
	1598	1603	1603	Aromatic stretching band
	1509	1510	1506	Aromatic ring
	1458	1459	1457	C-H deformation
	-	1328	-	Bending vibrations of OH
	1269	1219	1269	C-O stretching
(methoxyls)	1215	1117	1212	C-O stretching (phenolic hydroxyl groups)
	1031	1036	1032	C-O deformation (methoxyl groups)
	857	836	867	C-H out-of-plane deformation

Table 4. Bands assignments of the acetylated lignins.

Lignin	Peak wavenumber (cm ⁻¹)			
Acetylated lignin	K.pino	K.eucalipto	Organosolv	Band assignment
	3459	3460	3452	Stretching vibrations in O-H
	2940	2934	2941	CH stretching vibrations
	2838	2849	2843	Tertiary CH groups
	1762	1757	1755	Unconjugated carbonyls
	1597	1599	1602	Aromatic stretching band
	1505	1504	1504	Aromatic ring
	1460	1461	1458	C-H deformation
	1370	1370	1369	Bending vibrations of OH bonds
	1199	1213	1202	C-O stretching, aromatic (phenyl)
	-	1127	-	Dialkyl ether linkages
	1033	1038	1033	C-O deformation (methoxyl group)
	902	903	904	C-H out-of-plane deformation in ethylenic double bonds
	-	834	-	Trisubstituted aromatic ring

Fig. 2 shows the infrared spectra of the three unmodified lignins. Below we present an analysis of the recorded spectra of the lignin used in this study, based on assignments given by Faix²⁶, and Boeriu¹¹.

Figure 2. FT-IR spectra of non-acetylated lignins

All lignins show a broad band between 3400-3500 cm^{-1} with similar peaks for E. nitens and organosolv lignins (3423 cm^{-1}) and something different for P. radiata lignin (3414 cm^{-1}). These strong bands are attributed to the hydroxyl groups in phenolic and aliphatic structures. The bands centred around 2928 and 2937 cm^{-1} , predominantly arising from CH stretching in aromatic methoxyl groups and in methyl and methylene groups of side chains.

The spectral region below 2000 cm^{-1} is more difficult to analyse, since most bands are complex, with contribution from various vibration modes.

In the carbonyl region, weak to medium bands are found at 1712-1715 cm^{-1} that can be associated to unconjugated C=O, and conjugated carbonyl/carboxyl spectra at 1598-1603 cm^{-1} .

Aromatic ring bands and C-H deformation between 1506 and 1457 cm^{-1} are very similar for all lignin but the bending vibration of OH at 1328 cm^{-1} is only visible in E. nitens lignin. This band has been reported for syringyl ring of hardwood and non-wood lignins¹¹.

C-O stretching for methoxyl groups show similar bands in P. radiata and organosolv lignins (1269 cm^{-1}) although it is weaker in E. nitens at 1219 cm^{-1} .

Differences were also observed for the phenolic hydroxyl groups. The absorbance in E. nitens is a strong band at 1117 cm^{-1} while P. radiata and organosolv lignin show a less intense band at 1212-1215 cm^{-1} .

The spectral region at 1031-1036 cm^{-1} and below these wavenumbers, show similar weak bands for the three lignins originating from aromatic C-H deformation and C-H out-of-plane vibrations, respectively.

Infrared spectra of the acetylated lignin samples were compared to spectra of original samples to establish the extent of esterification reactions and the influence on thermal properties.

Esterification reactions resulted in the drastic reduction of the OH absorption band between 3400 and 3500 cm^{-1} , as shown in Fig. 3, along with the appearance of the main absorption bands 1750 and 1760 ($\text{C}=\text{O}$ stretch).

Another absorption band appears for E. nitens lignin at 1127 cm^{-1} probably due to syringyl ring.

Acetylated lignins are shown in Fig. 3

Figure 3. FT-IR of acetylated lignins.

Thermal properties of lignins

DSC is the most widely accepted method for determining glass transition temperature of lignin or modified lignin samples²⁷.

The Tg of dry lignin is often more difficult to detect than in a synthetic polymer, due to the complex structure of lignin and sometimes only is possible to detect the range of the change in the curve²⁸.

Figure 4 shows the DSC thermograms of unmodified lignins of E. nitens Kraft liquor, P. radiata Kraft liquor and organosolv lignin.

Figure 4. DSC thermograms of unmodified lignins.

The Tg of the three lignins do not exhibit significant differences, until 170° C and were determined from the change in the heating curve, previous to the degradation temperature.

The change in the curve for P. radiata lignin begins above 120°C, and at 100°C for acetylated lignin, (figure 5).

For E. nitens lignin, the change begins at 140°C. Acetylated lignin in the figure 5 shows a change at 120°C.

Figure 5 shows the glass transitions of partially acetylated lignins.

Figure 5. DSC thermograms of acetylated lignins.

Acetylated organosolv lignin shows a weak change of Tg at 122°C. In the non-acetylated organosolv lignin a clear change in the curve was not detected.

The Tg values are in the glass transition region reported in the literature for several types of lignins, between 110°C-150°C.^{29,30}

In Figure 5 the glass transition temperature for all the lignin acetates clearly decreases with respect to the unmodified lignins.

The acetylation reaction produces a plastification phenomenon in the lignin because a decrease in the intermolecular interactions between hydroxyl groups of lignin is observed and lower Tg values are obtained.

CONCLUSIONS

FT-IR analysis showed some differences between the spectra for the three lignins studied.

In E. nitens lignin the bending vibration of OH at 1328 cm^{-1} , can be attributed to the syringyl of hardwood and also the band at 2851 cm^{-1} attributed to tertiary groups are only visible in E. nitens lignin. These IR bands can be used as a fast technique to characterize this kind of lignin.

P. radiata lignin and organosolv lignin show a strong band at 1269 cm^{-1} which is attributed to CO stretching. This band is weaker in E. nitens lignin.

Differences were also observed for the phenolic hydroxyl groups. While the absorbance in E. nitens is a strong band at 1117 cm^{-1} a less intense band at 1212-1215 cm^{-1} is observed to P. radiata and organosolv lignins.

Acetylated lignins show an important decrease in the band at 3400-3500 cm^{-1} attributed to OH, while the band of CO stretches at 1750-1760 cm^{-1} increasing significantly.

Other absorption bands appear in acetylated lignins at 1370 cm^{-1} attributed to aliphatic C-C stretch probably from acetic anhydride incorporated to the

lignin molecule in the esterification reactions.

Lignin molecules are composed of phenyl propane units interconnected by about 10 different linkages in a complex matrix that are quite different from most synthetic polymers because of the high degree of association between their macromolecules. Due this, thermal behaviour and glass transitions were often difficult to detect especially in the case of non-acetylated lignins.

Glass transitions for non-acetylated organosolv lignin were indiscernible.

The Tg for the lignins is not easily detected by DSC and a faster heating rate is required to appreciate the weak change in the curve of the thermogram.

The thermal study of the lignins showed a similar behaviour for the glass transition temperature in the three types of lignins analyzed.

As has been reported in the literature, polymer plastification decreases the Tg value. This study shows that the acetylated lignins exhibit lower Tg values possible due to the reduction in the degree of intermolecular association occurring within the lignin. Lignin esterification decreases the availability of OH groups in the lignin molecule and the addition of nonreactive acetyl groups can also make the chains stand off from one another, reducing Tg.

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