

Utilization of Pine Kraft Lignin in Starch Composites: Impact of Structural Heterogeneity

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To elucidate the effect of lignin structure on the properties of lignin–starch composites, an industrial pine kraft lignin sample was fractionated by sequential extraction with organic solvents. Three fractions were obtained with different carbohydrate contents, infrared spectra, and molecular size distributions. In addition, an in-depth structural investigation was performed by GC–MS analyses of the low-molecular weight phenolics occurring in the native fractions or obtained by thioacidolysis. The properties of the lignin–starch composites made from pine kraft lignin or its fractions were evaluated, as compared to reference starch films. Although present in small quantities, the low-molecular weight fraction isolated from pine kraft lignin was observed to have a key role in the mechanical properties of the films, mainly as a starch plasticizer.

Keywords: *Lignin; starch; lignin utilization; lignin–starch composites*

INTRODUCTION

There is considerable interest in the nonconventional utilization of industrial lignins produced by pulp manufacturers. These worldwide efforts aim at improving the economical and/or environmental performances of biomass transformation process, through innovative uses of byproducts (Lindberg et al., 1989). In this line, the use of lignin as filler in starch films is currently under investigation, with several goals: the utilization of industrial lignins produced by the pulp and paper industry, the improvement of the starch matrix hydrophobicity, and the knowledge of starch–lignin interactions (Baumberger et al., 1997, 1998).

It is well established that the structure of isolated lignins determines not only their physicochemical properties, such as solubility and thermal softening (Yoshida et al., 1987; Kelley et al., 1988; Kubo et al., 1996), but also the behavior of lignin-based thermoplastic systems such as organosolve lignin-hydroxypropylcellulose (Rials and Glasser, 1989), sulfur free lignin–polypropylene (Kosikova et al., 1993), kraft lignin–polyvinyl acetate (Li et al., 1995), and lignosulfonates–polyolefins (Simionescu et al., 1996). In these studies, the effect of chemical modifications or hydrodynamic volume variations supports the causal relationship between lignin structure and the properties of lignin-based films.

The composition of kraft black liquors and the heterogeneous structure of dissolved kraft lignins have been repeatedly investigated (Gellerstedt and Lindfors, 1984; Mörk et al., 1986, 1988; Niemela, 1990; Gellerstedt and Zhang, 1991). However, the significance of this heterogeneity in the potential use of kraft lignins as filler in polymeric materials has not been examined. The present study aims at an in-depth investigation of distinct fractions recovered from pine kraft lignin, in

relation with the properties of lignin–starch films prepared from them.

This structural investigation was run not only by conventional techniques (infrared spectroscopy and gel permeation chromatography) but also by innovative strategies applied for the first time to kraft lignin fractions (determination of lignin-derived monomers and dimers released by thioacidolysis).

MATERIALS AND METHODS

1. Materials and Lignin Fractionation. Softwood kraft lignin (Indulin AT, 95% dry matter) was supplied by WEST-VACO (Charleston, SC). Wheat starch (type A, 87% dry matter, 27% amylose, 73% amylopectin) was commercially available (F33 Amylum Aquitaine, France).

The sequential solvent fractionation of the crude kraft lignin was performed according to the procedure of Mörck et al. (1988), using successively dichloromethane and methanol (pro analysis grade). Indulin AT (5–10 g) was suspended in 5:1 (v:w) dichloromethane and magnetically stirred for 30 min. The mixture was filtered and suspended again in fresh dichloromethane. The combined organic extracts were evaporated under reduced pressure by rotavapor leading to a viscous light yellow fraction F1. The insoluble material was extracted twice by methanol using the same procedure to recover a second fraction F2, as a dark brown powder. The last fraction F3 consisted of the final dark brown insoluble residue.

2. Analysis of Lignin and Its Fractions. The infrared (IR) absorption spectra of lignins were recorded from a potassium bromide disk by using a Perkin-Elmer IR 580 spectrometer between 4000 and 400 cm^{-1} .

Total sugar content was determined by the colorimetric phenol sulfuric method after hydrolysis (Dubois et al., 1955).

Gas Chromatography–Mass Spectrometry (GC–MS) Analysis of F1. After drying, 5 mg of F1 was redissolved in 1 mL of CH_2Cl_2 . An aliquot of this solution (10 μL) was silylated with 50 μL bistrimethylsilyltrifluoroacetamide (BSTFA) and 5 μL pyridine prior to GC–MS analysis. Gas chromatography was run on a SPB5 poly(5% diphenyl–95% dimethylsiloxane) capillary column (Supelco, 30 m \times 0.2 mm i.d., 0.25 μm) with

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helium as carrier gas (0.5 bar inlet pressure) and with a (180–260 °C at 2 °C/min) time program.

MS of dilignols identified in F1 and analyzed as their trimethylsilylated derivatives (electronic impact 60–650 *m/z* range, ion trap instrument): *Z*- or *E*-4,4'-dihydroxy-3,3'-dimethoxystilbene 416 (M^+ , 100), 401 (2), 386 (22), 356 (6), 253 (2), 222 (2), 178 (2), 89 (2), 73 (42); 2',4'-dihydroxy-5'-(3-hydroxypropyl)-3,3'-dimethoxystilbene 546 (M^+ , 100), 531 (2), 516 (6), 456 (2), 430 (11), 426 (3), 400 (4), 383 (2), 369 (2), 355 (2), 325 (2), 294 (2), 209 (2), 89 (3), 73 (42); secoisolariciresinol 650 (M^+ , not seen due to instrument upper mass limit), 560 (40), 470 (55), 439 (25), 350 (10), 261 (30), 247 (12), 235 (5), 223 (5), 209 (50), 179 (7), 103 (5), 89 (2), 73 (100).

Degradative Analysis of Lignins. Thioacidolyses were run as previously described by Lapierre et al. (1995): 5–10 mg of pine kraft lignin (KRL) or its fractions were heated in an oil bath at 100 °C for 4 h with 12 mL of dioxane/ethanethiol mixture (9/1, v/v), 0.2 M boron trifluoride etherate. After cooling, the reaction mixture was poured into CH_2Cl_2 to which the gas chromatography internal standard was added (docosane C22, 0.11–0.21 mg). The aqueous phase was adjusted to pH 3–4 with 0.4 M aqueous $NaHCO_3$ and the whole mixture was extracted with CH_2Cl_2 . The combined organic extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The resulting dry residue was redissolved in about 1 mL of CH_2Cl_2 prior to silylation and subsequent GC and GC–MS (electronic impact, 70 eV) analyses as previously described (Lapierre et al., 1995).

Desulfuration of the thioacidolysis samples was performed as follows: an aliquot of the thioacidolysis solution was put together with 1 mL of Raney nickel slurry (Aldrich, W2 type) and 5 mL of dioxane in a tube fitted with a Teflon-lined screwcap. The reaction was then allowed to proceed at 50 °C (oil bath) for 4 h. After cooling, the reaction mixture was poured in 30 mL of CH_2Cl_2 , adjusted to pH 3–4 and extracted with CH_2Cl_2 . The organic extract was dried over Na_2SO_4 and evaporated under reduced pressure. The residue was redissolved in about 200 μ L of CH_2Cl_2 , prior to silylation and GC or GC–MS as previously described (Lapierre et al., 1995). Analyses were made in duplicate, with 5–10% standard error.

High Performance Size Exclusion Chromatography (HPSEC). All lignin samples were acetylated prior to gel permeation whereas thioacidolysis products were directly analyzed. Acetylation was carried out using equal volumes of acetic anhydride and pyridine at room temperature for 60 h. The acetylated lignins were recovered by precipitation of the reaction mixture in cold water prior to centrifugation (4350 g). Excess acetylation reagent was removed by repeated azeotropic evaporations (Gellerstedt, 1992) prior to freeze-drying. Acetylated lignins were dissolved in tetrahydrofuran (THF). The solutions were filtered with a 0.45 μ m PVDF filter, prior to injection (10–20 μ L of 10 mg mL^{-1} solutions).

HPSEC of acetylated lignins was performed at room temperature using a 600 \times 7.5 mm PL-gel column (Polymer Laboratories, 5 μ m, mixed-C pore type) with THF (1 $mL\ min^{-1}$) as eluent and detection at 280 nm. A 600 \times 7 mm PL-gel column (Polymer Laboratories, 5 μ m, 100 Å) with a 1.5 $mL\ min^{-1}$ THF flow rate was used for HPSEC of thioacidolysis products. Polystyrene standards (M_w ranging from 800 to 1.8 $\times 10^6$) and eugenol (M_w 163) were used for relative calibration.

3. Film Casting and Characterization. Cast films with 80/20 starch/lignin ratio were prepared from KRL, F2, and F3, according to Baumberger et al. (1998). Samples cut from each film were stored at room temperature over a saturated sodium bromide solution (water activity $a_w = 0.57$ at 25 °C) prior to water determination (104 °C, 4 h) and tensile mechanical tests (INSTRON 1122 universal testing machine, stretching speed 0.2 $mm\ min^{-1}$). Elongation at break and stress at break were measured with 30% accuracy.

Water solubility was determined from the dry weight loss of a 50–100 mg film sample after a 24 h immersion in 40 mL distilled water at 25 °C. It was reported as the percentage of soluble matter in the sample on initial dry weight basis. The

Table 1. Comparison of Isolation Yield, Carbohydrate Content, and Thioacidolysis Yields of a Pine Kraft Lignin Sample (KRL) and Its Fractions

	KRL	F1	F2	F3
isolation yield, % of initial dry lignin		0.3	44.6	52.6
carbohydrate content, %	1.8		0.6	3.1
thioacidolysis yields, μ mol g^{-1}				
G (C_6C_3)	131.4	56.7	95.3	168.4
G enols (C_6C_2)	31.3	48.7	35.3	41.4
C catechols (C_6C_3)	12.6	traces	10.4	10.4
G dimers	63	426	87	54

amount of phenolic compounds dissolved in water was evaluated by measuring the absorbance of the filtered suspension at 280 nm and reported as the percentage of soluble phenolics on lignin dry weight basis. The absorption coefficient ϵ used for concentration calculation was 26 $g^{-1}\ L\ cm^{-1}$, as previously determined on a KRL solution in 50/50 (v/v) aqueous dioxane. Solubility tests run on two samples belonging to the same film indicated $\pm 5\%$ variations, in terms of water solubility and soluble phenolics.

RESULTS AND DISCUSSION

Isolation Yield and Carbohydrate Content of Kraft Lignin Fractions. The solvent fractionation protocol readily allowed isolation of substantial amount of the lignin fractions (several tens of grams) in order to perform casting experiments. The procedure used by Mörk et al. (1986) to fractionate softwood kraft lignins was simplified in order to obtain only three fractions with distinct features. Fractionation yields are shown in Table 1. Fractions F2 and F3 are obtained in similar yields and account for almost all the initial material. In contrast, the dichloromethane soluble fraction F1 represents less than 1% of the initial material. Global carbohydrate determination (Table 1) indicates that fraction F3 is enriched in carbohydrates (3.1% content versus 1.8% for the unfractionated lignin). These carbohydrates most likely consist of hemicellulosic or hemicellulosic-derived compounds, adsorbed or grafted onto lignin as a consequence of alkaline pulping (Kleinert, 1965).

Infrared Spectroscopy. The three lignin fractions have similar IR spectra, typical of softwood lignins (Hergert, 1971; Faix, 1992). A close examination reveals significant differences in some areas which are outlined in Figure 1. The F1 spectra is typified by a strong band between 1650 and 1750 cm^{-1} with a maximum at 1695 cm^{-1} corresponding to conjugated carbonyl stretching. This band is less pronounced in the spectra of F2 and occurs as an ill-defined shoulder in F3. This result suggests a high carbonyl content in F1, in agreement with Mörk et al. (1986). Between 1200 and 900 cm^{-1} , the spectra differ in the resolution between the two bands at 1150 and 1120 cm^{-1} , corresponding to aromatic C–H in-plane deformation and to C–O and C–C stretching of the carbohydrates associated to lignin.

Gel Permeation of Acetylated Lignin Samples. The comparison of the HPSEC profiles of the lignin samples (Figure 2) indicates that lignin fractions differ both in average hydrodynamic properties, or “size”, and polydispersity. As expected from the work of Schuerch (1952), the molecular size of the fractions increases when the hydrogen bonding capacities of the solvent used for fractionation increases. Moreover, the narrowest molecular weight distribution is obtained with the lowest molecular size fraction F1, as previously observed (Mörk et al., 1986; Thring et al., 1991). Calibration with

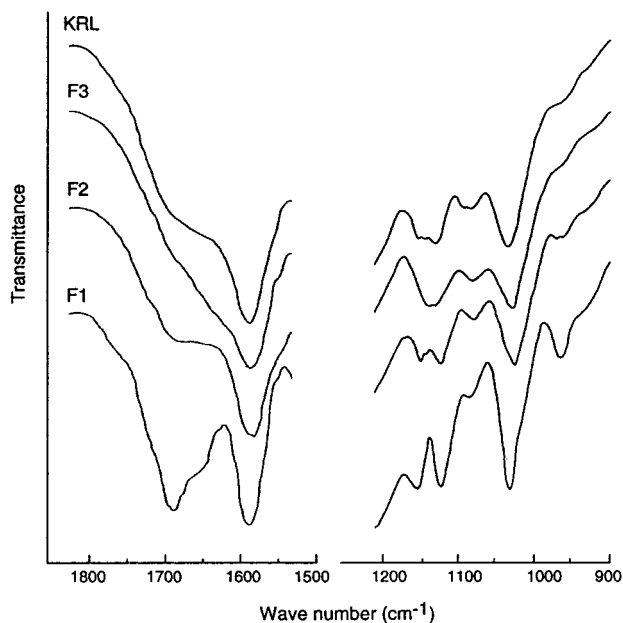


Figure 1. Partial infrared spectra of pine kraft lignin and its fractions. Transmittance is expressed in arbitrary units (a.u.).

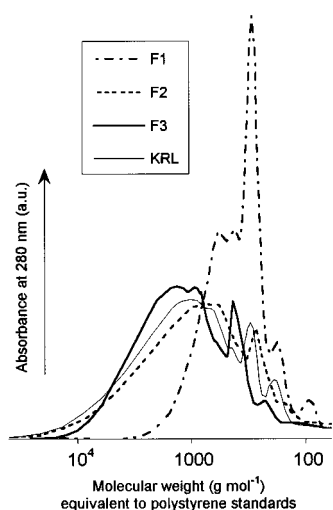


Figure 2. Molecular size distribution of a pine kraft lignin sample (KRL) and its fractions after acetylation. For comparison, each profile was normalized by its total area.

polystyrene standards suggests that F1 mainly consists of oligomeric compounds whose average molecular weight does not exceed the molecular weight equivalent of 800 g mol^{-1} , which roughly corresponds to four C_6C_3 building units.

GC-MS Analysis of Fraction F1. The HPSEC analyses suggest that F1 is enriched in low-molecular weight compounds. Accordingly, these compounds were directly analyzed by GC-MS of their silylated derivatives (Figure 3). The GC-MS identification was run according to previously published mass spectra (Eckman, 1976; Niemela, 1989, 1990; Reunanen et al., 1989). The identified compounds are mono- or dilignols, resinic acids, and free fatty acids. The major component is a β -1 stilbene (4,4'-dihydroxy-3,3'-dimethoxystilbene), previously described by Niemela (1990). The β -1 and β -5 stilbenes may originate either from the loss of C_γ hydroxymethyl groups in diarylpropane and phenylcoumaran structures, respectively, or from aryl migrations associated with β -aryl ether cleavages (Gierer, 1992).

The secoisolariciresinol dimer was tentatively identified by comparison with the mass spectral data of Eckman et al. (1976). In addition to these dilignols, a series of monolignols could be evidenced. Dihydroconiferyl alcohol, guaiacol, vanillin, vanillic acid, and acetovanillone are the main monolignols constitutive of F1. They stem from solvolytic and oxidative degradations of lignin during pulping. The presence of catechol in noticeable amount is indicative of demethylation. Various fatty acids could be identified together with resinic acids, with a predominance of palmitic, oleic, abietic, and dehydroabietic acids. These aliphatic compounds constitutive of softwoods are dissolved as sodium salts in the cooking liquor. The evidence of various low-molecular weight compounds with carbonyl and carboxylic groups in the F1 fraction is in agreement with the data from IR characterization. Moreover, a high content in free phenolic groups can be predicted for F1 from the structure of mono- and dilignols, in agreement with the functional group determination by Mörk et al. (1986).

Thioacidolysis Yields. Kraft lignin and its fractions were compared by mean of thioacidolysis in terms of monomer yield. Not unexpectedly, the lignin-derived monomers released by thioacidolysis of the crude pine kraft lignin belong to the guaiacyl and catechol series and only traces of syringyl units could be detected. Both C_6C_3 monomers, essentially provided by glycerol- β -aryl ethers, and C_6C_2 monomers, mainly originating from enol ethers, were quantified for the guaiacyl (G) and catechol (C) series (Table 1). The signatures of enol and catechol structures are similar in the F2 and F3 fractions. In contrast, fraction F1 shows only trace amounts of catechol structures and a relatively high proportion of enol ethers. Besides, the C_6C_3 G monomer released from guaiacylglycerol- β guaiacyl ethers is recovered in different yields, increasing from F1 to F3. The low yield observed for F1 may reflect its low content in β -O-4 bonds and the abundance of α -carbonyl groups, as revealed by GC-MS. The higher yield of F3 is still far below that obtained from native lignin (ca. $1000 \mu\text{mol g}^{-1}$ lignin for G(C_6C_3), Rolando et al., 1992), as a consequence of β -O-4 bonds cleavage and recondensation reactions under alkaline pulping. However, this yield indicates that an appreciable amount of β -O-4 structures survives the severe conditions of kraft cook.

HPSEC provided further information about the size distribution of the condensed thioacidolysis mixture (Pasco and Suckling, 1994). Profiles relative to crude lignin and to each fraction are compared in Figure 4. Star indicates the peak corresponding to the main thioacidolysis monomers. The relative amount of high molecular weight thioacidolysis compounds increases from F1 to F3, concomitantly to the average molecular weight of the native fraction.

Desulfuration after thioacidolysis allowed identification and quantification of the main phenolic dimers representative of resistant interunit bonds. The global yield of G dimers relative to each lignin sample is given in Table 1. Dimers were identified on the basis of their mass spectra according to previous studies (Lapierre et al., 1991, and Table 3). Their structure and relative frequency are given in Figures 5 and 6. The unfractonated lignin mainly leads to β -1 and β -5 dimers. These dimers recovered after thioacidolysis and desulfuration stem both from diarylpropane and stilbene structures. Dimers of the 5-5, β -6, and 4-O-5 types are also detected, in lower amount, together with a tetrahy-

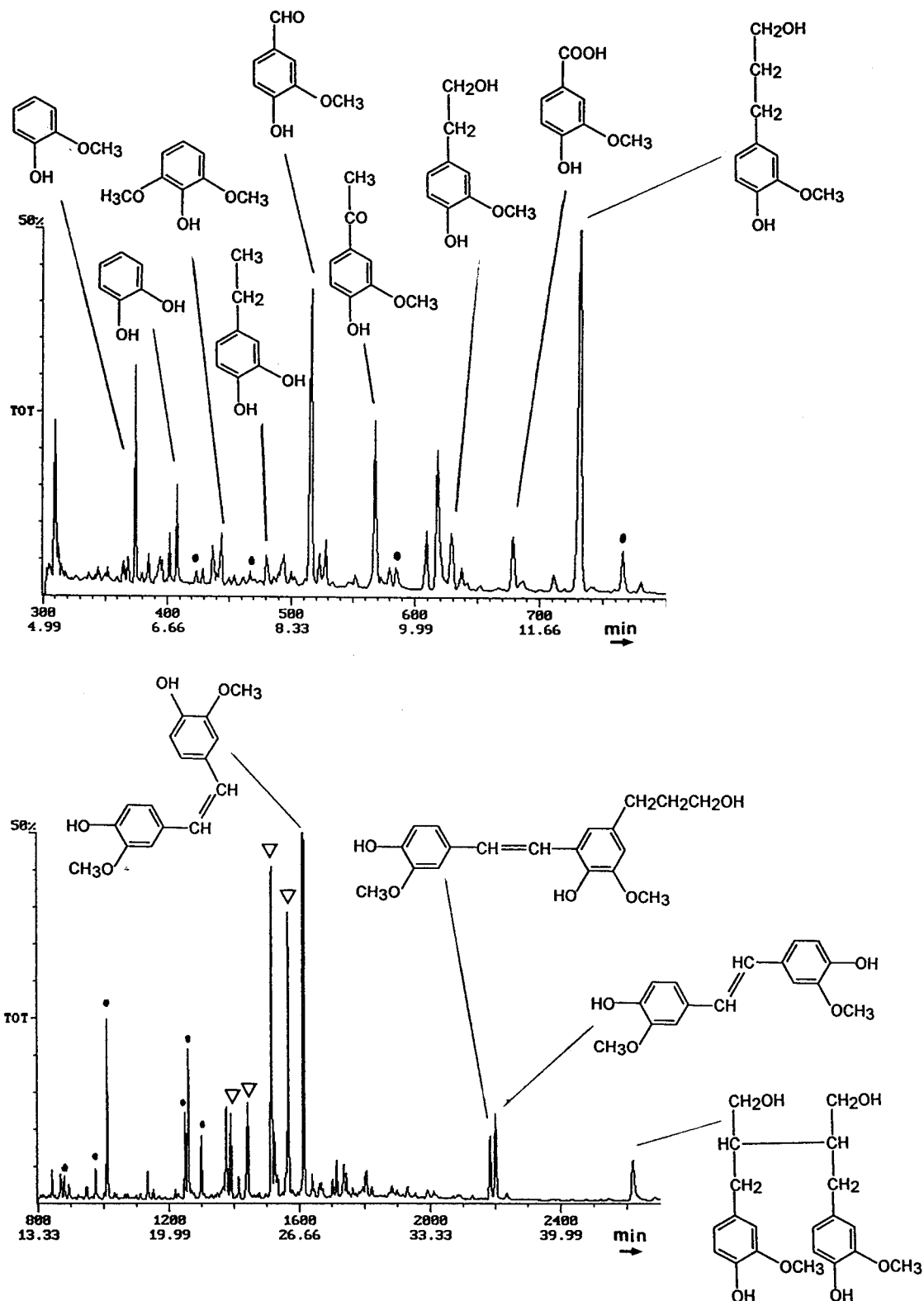


Figure 3. GC-MS total ion chromatogram showing the main mono- and dilignols identified in the fraction F1 after silylation. For convenience, compounds are shown in their underivatized form. Specific marks indicate the peaks corresponding to resinic acids (∇) and fatty acids (\bullet).

drofuran dimer which typifies softwood lignins. Fraction F1 is characterized by a high yield of dimers, of which 72% belong to the β -1 series. This result is in agreement with the abundance of free stilbenes in F1. F2 and F3 markedly differ from each other in terms of the relative abundance of β -1 dimers. Indeed, F3 is enriched in condensed linkages of the β -5, 5-5, β -6, and

4-O-5 types, β -1 structures accounting only for 16% of the total dimers versus 54% in F2. β -1 structures were shown to appear at the earlier stage of the pulping process (Lapierre et al., 1994). Thus, the dimeric distribution relative to F3 suggests that this fraction corresponds to the lignin dissolved in the last stage of pulping. Moreover, the enrichment in β -6, β -5, and 5-5

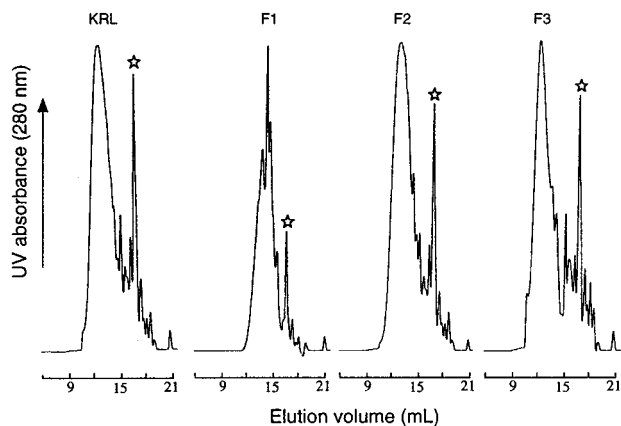


Figure 4. HPSEC traces of thioacidolysis products from pine kraft lignin and its fractions. All traces are scaled so that the higher peaks are of equal height. The peak due to thioacidolysis monomers is marked with a star.

Table 2. Properties of 80/20 Starch/Lignin Films Obtained from a Pine Kraft Lignin Sample (KRL) and Two of Its Fractions Compared to a Reference Starch Film

	starch	starch/ KRL	starch/ F2	starch/ F3
water content, %/dry weight	11.6	10.2	9.8	11.1
stress at break, MPa	2.3	2.5	2.4	very brittle
elongation at break, %	0.2	2.0	0.4	very brittle
water solubility, %/initial dry weight	15.7	16.2	12.6	17.6
soluble phenolics, %/lignin dry weight		5.6	9.4	2.8

dimers may be indicative of recondensation reactions, in agreement with gel permeation analysis.

Influence on the Properties of Lignin–Starch Films. To investigate the influence of lignin structure on the behavior of starch-based materials, KRL together with fractions F2 and F3 were used to produce 80/20 (by weight) starch/lignin films. It is known from previous microscopic observations (Baumberger et al., 1998) that KRL/starch films have a heterogeneous structure consisting of about 1 μm lignin particles dispersed in a starch-rich matrix. In addition, fluorescence microscopy revealed that some phenolics were miscible with starch. Some mechanical properties were also reported, suggesting that lignin heterogeneity plays an important role. These results are discussed now in light of the current structural investigation.

The comparative evaluation of lignin/starch films prepared from KRL or its fractions and of a reference

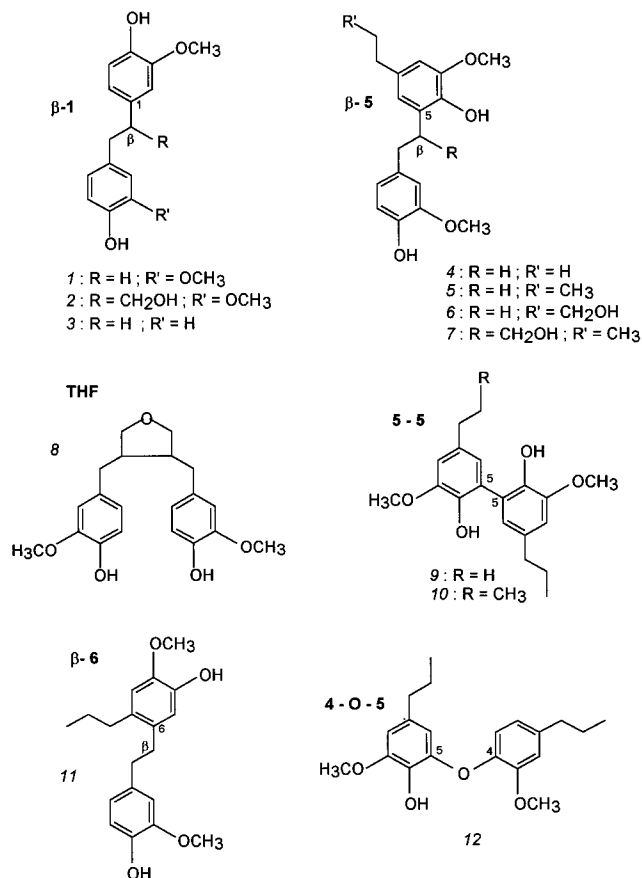


Figure 5. Structure of the identified and quantified dimers recovered from thioacidolysis of a pine kraft lignin sample (KRL) and its fractions after desulfuration over Raney nickel.

film made from pure starch (Table 2) provides original information on the key lignin structural features that drastically influence the film properties. The incorporation of the high molecular weight lignin fraction F3 detrimentally affects the film mechanical properties, leading to a very brittle material. This behavior may reflect the severe incompatibility between F3 and starch. In contrast, F2 has no clear-cut effect on the film mechanical properties, reflected by stress and elongation at break, which are similar for starch film and F2/starch film. In addition, F2 slightly reduces the water content and the water solubility of the film. Concomitantly, the amount of water-soluble phenolics released from F2/starch films is higher than with F3. These hydrophilic compounds are likely to interact with the starch matrix, through hydrogen bondings, and to

Table 3. Abbreviated Mass Spectra (Electronic Impact, 70 eV Quadrupole Instrument) of the TMS Derivatives of Lignin-Derived Dimers Recovered after Thioacidolysis Then Desulfuration of Pine Kraft Lignin Fractions^a

TMS of	M ⁺	other ions
1	418 (10)	403 (3), 209 (100), 179 (10), 73 (70)
2	520 (5)	505 (2), 430 (2), 417 (4), 311 (50), 223 (10), 209 (25), 192 (10), 179 (15), 149 (10), 73 (100)
3	388 (50)	373 (10), 209 (100), 179 (60), 149 (3), 73 (80)
4	446 (25)	431 (5), 237 (20), 222 (10), 209 (100), 207 (10), 193 (5), 179 (5), 73 (40)
5	460 (25)	445 (5), 251 (20), 236 (5), 209 (100), 207 (15), 193 (5), 179 (10), 73 (60)
6	548 (20)	533 (5), 472 (2), 458 (5), 398 (10), 339 (10), 223 (10), 209 (100), 193 (8), 179 (10), 89 (5), 73 (100)
7	562 (8)	472 (4), 352 (5), 263 (5), 209 (35), 191 (30), 73 (100)
8	488 (50)	473 (3), 209 (75), 193 (10), 179 (30), 73 (100)
9	460 (35)	445 (15), 431 (5), 430 (5), 178 (5), 147 (5), 73 (100)
10	474 (40)	459 (10), 445 (5), 444 (4), 385 (5), 358 (5), 178 (5), 147 (5), 73 (100)
11	460 (25)	445 (5), 251 (100), 223 (10), 220 (10), 209 (25), 193 (8), 179 (10), 73 (40)
12	402 (90)	387 (40), 373 (25), 372 (25), 357 (10), 343 (15), 209 (10), 157 (20), 73 (100)

^a The numbers refer to structures depicted in Figure 5.

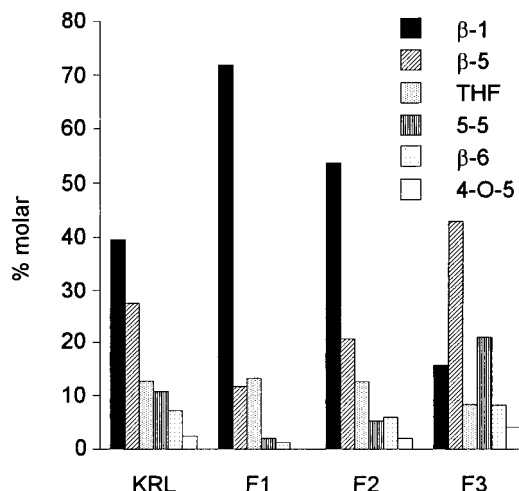


Figure 6. Relative frequency of the G dimers identified in Figure 5 recovered after thioacidolysis and desulfuration of pine kraft lignin.

consequently increase its adherence to lignin domains. The whole KRL lignin shows an intermediate behavior, with regards to water solubility and water content. A very substantial effect of KRL lignin is the 10-fold increase in elongation at break, compared to the starch reference. Taken together, these results point to the dramatic influence of the low-molecular weight phenolics, responsible for an increased plasticity of the starch matrix: their removal, as fraction F1, makes this plasticizing effect collapse. Common plasticizers for starch-based plastics are polar molecules including water, glycols, sugars, and amides. Stein and Green (1997) have recently reported the ability of some amino acids to plasticize starch, even at relatively low concentrations. Among the constituents identified in F1, hydroxyl or carbonyl rich lignols together with amphiphilic fatty acids are very likely to interact with polysaccharides. Furthermore, the variety of molecular species constitutive of KRL may result in a cumulative plasticizing effect, as recently observed with urea and glycols in gelatinized starch (Shogren et al., 1992).

CONCLUSION

This structural investigation supports earlier findings that kraft lignin is a heterogeneous group of molecular species. Sequential organic solvent solubilization allowed recovery of three fractions with distinct molecular sizes, functionalities, and distribution of main interunit bonds.

The structural features of these fractions closely reflect the successive changes in the structure of dissolved lignins during kraft cooking. F1 mainly represents the low-molecular weight fragments dissolved during the initial delignification stage. On the other hand, the last fraction F3 embodies the condensed, carbohydrate-enriched lignin dissolved in the final delignification stage. The intermediate methanol soluble fraction F2 may correspond to the bulk delignification step. Besides its significance relative to kraft cooking mechanisms, lignin heterogeneity was shown to play an important role in the behavior of starch/lignin composites. Although representative of a minor portion of pine KRL, low molecular weight compounds seems to be primarily involved in plasticization or compatibilization phenomena.

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