Lignin-based Phenol-Formaldehyde Resins from Purified CO_2 Precipitated Kraft lignin (PCO_2KL)

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Abstract

To investigate the potential for using purified CO_2-precipitated Kraft lignin (PCO_2KL) with phenol-formaldehyde (PF) for application as an adhesive in plywood production, two lignin replacement procedures were examined to assess lignin's effect on bond quality. Methylolation and oxidation with hydrogen peroxide (H_2O_2) were carried out to try to increase lignin reactivity. The first procedure involved substitution of 30% of the PF resin solids in the adhesive mix with a solution of methylolated lignin with or without prior oxidation; the second replacement procedure involved direct condensation of lignin or oxidized lignin to replace 25% of phenol. Formulated adhesives were compared to a control phenol-formaldehyde (PF) adhesive prepared in the laboratory. The physical properties (solid content, viscosity and pH values) of formulated resins were determined. PCO_2KL-based adhesives showed comparatively good plywood shear strengths. However, they had lower wood failures than those of test samples made from PF resin only.

Keywords: Kraft lignin; lignin-phenol-formaldehyde resin; hydrogen peroxide; methylolation; physical properties; shear strength; wood failure

Introduction

Phenol-formaldehyde (PF) resins are generally synthesized using fossil fuel chemicals of phenol and formaldehyde under alkaline conditions. PF resins have high mechanical strength and good at preventing delamination. They are extremely resistant to moisture and have excellent temperature stability (Cetin and Ozmen 2002). They are often used as adhesives for exterior-grade panels in housing cement templates, and container floors, for example. Although PF resins have many excellent properties, the high price of phenol, a dark color, and high cure temperature restrict their broader application. Reduction of cost and substitution of fossil fuel-based raw materials are an important direction for development of PF adhesives.

Lignin, the most abundant natural polyphenol, has been incorporated into wood adhesives due to its similar structure to PF resins (Turunen et al. 2003; Tejado et al. 2007). The abundance of different types of lignin as a by-product in pulp mills has made such materials an attractive proposition for the preparation of adhesives. Kraft lignin (KL), a phenolic polymer formed during the Kraft pulping process, is presently burned as a low-grade boiler fuel to provide heat

and power to the process (Huber et al. 2006). For decades, researchers have attempted to use KL as an inexpensive substitute for phenol in phenol-formaldehyde (PF) resins, but KL use in PF resins is limited. Two main factors involve economical and technical reasons. It is likely that lignin's application is limited by its complex structure, variable composition, and its low reactivity compared to phenol. The functional groups on the aromatic ring in lignin are mainly methoxy or other ethers, with little phenolic or alcoholic –OH groups. There are few para- and ortho- reactive sites in lignin molecules and poor accessibility of these sites lead to limited cross-linked structure and low solubility. Kraft lignin solutions are complex mixtures which have broad molecular weight distributions, high viscosities, relatively low reactivity, and low solubility. If lignin is added to other polymer systems as a separate phase, it will become a weak spot that causes defects and cracks, and reduces the other polymer's overall mechanical performance. Attempts to overcome these inherent problems include methylolation of lignin to improve reactivity, the use of co-solvents to improve solubility, and ultrafiltration to yield more homogeneous molecular weight fractions. The difficulties in lignin manufacturing, recovery, purification, and uniformity of reactivity all impose obstacles for the development of its new applications (Vishtal and Kraslawski 2011).

Two main pathways have been reported for the preparation of Lignin-phenol-formaldehyde (LPF) resin: first, lignin is purified (Wang et al. 2009; Jin et al. 2010) and modified to obtain high purity and reactive products, which can be used in the preparation of phenolic resins. There are three major modification strategies: methylolation (Vazquez et al. 1997; Goncalve and Benar 2001), phenolation (Ma et al. 2011; Lee et al. 2012) and demethylation (Olivares et al. 1988). Although the activity of lignin increases after purification and modification, the cost of production also increases. The second pathway is the so called "catch all" pathway (Stewart 2008) that utilizes the entire raw lignin without purification (Cetin and Ozmen 2002; Cavdar et al. 2008). However, these latter lignin materials have low reactivity. As a result, LPF adhesives made from them need higher temperature or longer time to be hot-pressed, which adds to the difficulty in industrial applications. With the recent industrial interest in them, further improvements are sought.

The viability of biofuel production would be greatly enhanced by development of markets for lignin-derived products. Any value-added lignin-derived products would improve the economy of biomass conversion (Doherty et al. 2011). Hence, in the biorefinery processes, apart from optimization of the enzymatic hydrolysis and fermentation parameters, full utilization of the residues is a feasible method to reduce cost (Jin et al. 2010). A newer potential route is the carbon dioxide precipitation of lignin from the Kraft black liquor (Nagy et al. 2010). This removes much of the lignin from the black liquor allowing further concentration prior to burning in the recovery boiler. Benefits are more efficient use of the recovery boiler and having a lignin product for other uses. The key to success of LPF is to tailor the reactions so that the modified lignins will co-react with the phenol and formaldehyde to make suitable adhesives. With Domtar announcing commercial production of a purified version of this lignin (PCO_2KL), this study evaluated its suitability as replacement in the preparation of PF resins.

Materials and Methods

Raw materials

The purified CO_2 precipitated lignin (Biochoice™ lignin) derived from southern pine (*Pinus palustris*) was supplied by Domtar, Plymouth Mill, NC United States. The PCO_2KL was oven dried for 24h at 50°C to remove water before use.

PCO_2KL oxidation with hydrogen peroxide under alkaline conditions

For oxidation under basic conditions, approximate 6 g of oven dried lignin and 30% H_2O_2 solution were loaded into 4% NaOH solution using different amounts of H_2O_2. Table 1 presents the details of the experimental conditions. Reaction was initiated by immersing the reactor into a preheated water bath. After the reaction, the reactor was quenched in a cold water bath. The reaction products were first precipitated by acidification to pH≈2 with H_2SO_4. The precipitated lignin was filtered, washed, and dried.

Table 1. Oxidation of PCO_2KL under alkaline conditions

	Reaction No.						
	1*	**2**	**3**	**4**	**5**	**6**	**7**
Temperature (℃)	70	70	90	90	90	100	100
Time (min)	20	20	10	20	20	10	20
Lignin (g)	6	6	6	6	6	6	6
30%H_2O_2 (g)	16	32	16	16	32	16	16
2%NaOH (g)	2	3.6	2	2	3.6	2	2
Distilled water (g)	95	130	95	95	130	95	95
Solids (%)	10	10	10	10	10	10	10

*The numerals in bold in the figure represents different oxidation treatment conditions

UV spectroscopy analysis

The phenolic hydroxyl content of the PCO_2KL before and after hydrogen peroxide oxidation was determined by UV spectroscopy. UV-spectroscopic methods are based on the wavelength shift between ionized and protonated phenolic hydroxyl groups. In alkaline solutions, phenolic hydroxyl groups are ionized and the absorption changes towards longer wavelengths and higher intensities. By subtracting the spectrum derived from the neutral solution from that of the alkaline solution, an ionization difference spectrum, a $\Delta\varepsilon_i$-spectrum is obtained. In this study, a Lambda 900 double-beam UV spectrophotometer was used. The alkaline solution is placed in the sample cell and the neutral solution in the reference cell. In this way, the difference spectrum can be measured directly. The spectra were recorded from 200 nm to 800 nm using a path length of 10 mm and a bandwidth of 1.0 nm.

A pH 12 buffer solution was prepared by diluting 12.4 grams of boric acid to 2 liters with 0.1N sodium hydroxide solution. A pH 6 buffer solution was prepared by mixing 495 ml of 0.2N potassium dihydrogen phosphate solution with 113 ml of 0.1N sodium hydroxide solution and

diluting to 2 liters with distilled water. A solution containing 0.1 g of sample per 100 ml pH 12 buffer solution was prepared. As soon as the sample was completely dissolved, 2.0 ml portions of the solution were diluted to 50.0 ml with pH 12 buffer solution; another 2.0 ml portion of the solution was diluted to 50.0 ml with 2.0 ml of 0.1N sulfuric acid and pH 6 buffer solutions.

PCO_2KL methylolation

Methylolated PCO_2KL was prepared using the procedure of Gardner and Sellers (1986) with some modifications. The solution composition for methylolating is shown in Table 2.

Sodium hydroxide (50%) was mixed with distilled water and heated to 80°C in a 250 ml flat bottom flask. The reaction was equipped with a magnetic stirrer, a thermometer and a reflux condenser. The lignin was slowly added to the sodium hydroxide solution and allowed to mix for 30 min. After the lignin solution was mixed, the temperature was reduced to 25°C and the formaldehyde is added during this cooling period. The resulting lignin solution is allowed to react for 72 hours at ambient temperature.

Table 2. PCO_2KL methylolation solution composition (42% (nonvolatile (NV)))

Ingredients	Parts by weight
Distilled water	35.21
NaOH, 50%	10.10
Dried PCO_2KL (with or without H_2O_2 oxidation)	36.04
Formaldehyde, 37%	19.63
Total	100.98

PF resole preparation

Pure resol was prepared following the formulation shown in Table 3.

Table 3. Formulation for pure resol preparation

PF Portion	MW(g)	Purity	Mass	Solids	Moles
Phenol	94.11	1.00	33.75	33.75	0.36
CH2O	30.03	0.37	60.42	22.36	0.75
50%NaOH-1	40.00	0.50	4.02	2.01	0.05
50%NaOH-2	40.00	0.50	1.81	0.90	0.02
water	18.00	1.00		10.05	
Totals			100.00	48.97	

The pure resol was prepared by charging cold phenol to a flat bottom flask, and then adding formaldehyde as rapidly as possible. The compounds were heated to 25°C over 5 min and then 50% NaOH-1 was charged dropwise with cooling. The compounds were then heated to

70(±1) ℃ over 15 minutes and held at 70(±1) ℃ for 1 hour. After that, 50% NaOH-1 was added as quickly as possible. The reaction was heated to 85(±1) ℃ over 15 minutes. After 45 minutes at 85(±1) ℃ sampling was begun for Gardner viscosity (A measurement of viscosity via the rise of an air bubble compared to standard samples). Temperature was maintained at 85(±1) ℃ until the viscosity of the sample reached a value of about 375-400 cP at 25 °C. When the desired viscosity was reached, the reaction was then stopped by rapid cooling of the reactor contents. The pure resol was then stored in refrigerator for further use.

The lignin-modified phenolic resin was prepared by replacing 25% of the phenol with PCO_2KL or oxidized PCO_2KL during the synthesis.

Adhesive mix procedure

The adhesive used in the manufacturing of plywood was prepared by mixing 70% of pure resol and 30% of methylolated PCO_2KL or 30% of methylolated oxidized PCO_2KL.

Table 4. Adhesive mix procedure

	Sample description
A	PF-resin standard
B	70% PF-resin +30% methylolated PCO_2KL
C	70% PF-resin +30% methylolated H_2O_2-oxidized PCO_2KL
D	25% phenol replaced with PCO_2KL
E	25% phenol replaced with H_2O_2-oxidized PCO_2KL

Viscosity

The viscosity of the resin samples was measured using a low-shear, rotating spindle apparatus (Brookfield Model DV-II+ Viscometer, Danvers, MA). Viscosity was estimated (cP) at a constant temperature (25 °C).

pH measurement

The alkalinity or acidity of solutions has a major effect on many adhesives properties. Properties such as viscosity, aging stability of the liquid adhesive, and properties of the adhesive bond such as water resistance are highly pH dependent. The acidity (pH) of the adhesives was measured. Three ml of each adhesive was dispensed into clean glass vials and stirred for 30 s. The pH values were measured at room temperature (22-25 °C) using a digital pH meter (HORIBA D-51, Kyoto, Japan).

Solids content

The solids content of the resins was determined by measuring the weight before and after removing the solvent by heating at 150°C for 30 min.

%solidscontent = (weight of the solid resin/weight of the solution) x100

Adhesive strength

The adhesive strengths of lignin-modified resin for wood-wood system were measured by the lap-shear method and compared with that of phenolic resin following ASTM D-906-98. Three-ply poplar plywood panels (152x152 mm) were made from veneers 3.3 mm thick. Adhesive was applied by roller and each veneer weighed to record the actual adhesive applied. The spread rate of the adhesive was 130 g/m2 on a dry weight basis (Cetin and Ozmen 2002). Assembly time consisted of 5 min. open time, 10 min. closed time, and 5 min. hot-press at 180°C, 150 psi. Veneers were preconditioned at 80°C/30% RH for 7 days before cutting and testing. Shear tests were done according to ASTM D 906-98 with five dry and five wet specimens from each board. Notches were cut in the specimens to ensure that the adhesive layers were subjected to loading, the lathe checks in the center ply of half the specimens were pulled open (tension), while in the other half the lathe checks were pulled closed (compression).

Discussion

UV spectroscopy

The UV difference spectra of the PCO_2KL oxidized by hydrogen peroxide, to determine the phenolic group content, are shown in Figure 1. The ionization difference spectra were obtained by subtracting the spectrum of lignin sample recorded in neutral solution (pH=6) from that recorded in alkaline solution (pH=12).

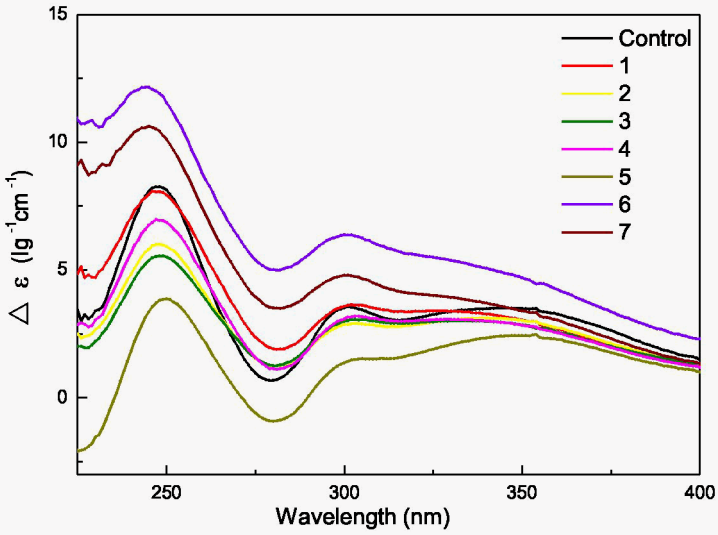

Figure 1. UV difference spectra of hydrogen peroxide oxidized PCO_2KL in neutral and alkaline solutions. (Numbers refer to products from reactions listed in Table 1)

Difference spectra were plotted in terms of absorptivity obtained by dividing the absorbance readings by the concentration of the diluted solutions in grams per liter. The intensities of the absorbance in the ionization difference spectrum are proportional to the content of phenolic hydroxyl groups. The method chosen for this work is based on the intensities of two maxima (250 and 300 nm) in the ionization difference UV spectrum. It is well established that the maxima at approximately 250 and 300 nm of difference curves are characteristic for the absorption of the phenolate ion of simple substituted aromatic hydroxyl compounds. Alkaline solutions of phenolic compounds in which the hydroxyl groups are conjugated through the ring with a carbonyl group have maxima near 250 and 300 nm. Thus, while the 250 nm maximum is common to both types of compounds, the 300 nm maximum of the difference curves is characteristic for phenolic hydroxyl groups without such conjugation. It can be seen from Figure 1, the phenolic hydroxyl groups increased after oxidation with treatments 6 and 7. The highest content of hydroxyl groups was obtained when the lignin was treated with the conditions of No.6. The treatment condition No.6 was used in this study for the oxidation of the lignin for plywood test.

Adhesive characterization

In order to distinguish and clarify the characteristics of the lignin-modified phenolic resins studied in this work, it is necessary to compare certain important properties with those of other similar resins. The resulting resins were characterized for their pH values, solid content, and viscosity. The characteristics of these lignin-modified phenolic resins are summarized in Table 5.

Table 5. Adhesive characterization

Experiment No.	pH values	Solid content (%)	Viscosity
A	10.98	52.72	1145
B	10.91	47.68	1700
C	10.49	46.31	810
D	10.58	51.69	668
E	10.47	53.21	472

Adhesive strength

A lap-shear test was performed to study the wood-wood adhesion using the lignin-modified phenolic resins. For comparative study, the same test was carried out for the pure PF resol. The data are presented in Table 6. Table 6 shows that the adhesive strengths for lignin-modified resins are lower than that of pure PF resol, and also that the wood failure decreased remarkably.

But by replacing 30% of PF resol with methylolated H_2O_2 oxidized PCO_2KL, or replacing 25% phenol with PCO_2KL or H_2O_2 oxidized PCO_2KL, the adhesive strength is retained at almost the same level with that of pure PF resol. The lower shear strength of the samples C, D and E might be attributed to over penetration of adhesive because of the lower viscosity of these samples. The wet plywood panels showed lower shear strength and wood failure in all cases but, strength retention of samples B and C after wet test was in general higher, thereby indicating promise of modified adhesives for plywood use where it is subjected to alternate drying and wetting at higher humid conditions.

Table 6. Shear strength and wood failure of plywood under dry and wet conditions

	Dry				Wet			
Experiment No.	Shear Strength (Psi)	Decrease	Wood Failure (%)	Decrease	Shear Strength (psi)	Decrease	Wood Failure (%)	Decrease
A	263 (±34)	0.0%	40(±24)	0.0%	232 (±49)	0.0%	27 (±12)	0.0%
B	186 (±89)	-29.2%	10 (±20)	-76.0%	197 (±62)	-15.0%	3 (±4)	-90.4%
C	219 (±75)	-16.7%	10 (±9)	-74.5%	213 (±68)	-8.1%	4 (±2)	-89.6%
D	256 (±64)	-2.67%	11 (±16)	-72.0%	181 (±62)	-21.9%	7 (±10)	-74.8%
E	229 (±67)	-12.9%	2 (±1)	-96.0%	169 (±65)	-26.8%	11 (±9)	-57.8%

Conclusions

The results of this investigation shows promise for partially replacing phenol by PCO_2KL in phenol formaldehyde resin designed for application as an adhesive in the production of plywood. PCO_2KL-based adhesives showed comparatively good plywood shear strengths for a low viscosity adhesive with no filler with substitution of 30% of the PF resin solids in the adhesive mix with a solution of methylolated lignin with or without oxidation; or direct condensation of lignin or oxidized lignin to replace 25% of phenol. However, PCO_2KL-based adhesives showed lower wood failures than those of test samples made from PF resin only. Lignin oxidation with H_2O_2 could be a good choice to improve the reactivity properties of lignin. H_2O_2-oxidized PCO_2KL-based adhesives showed a little better plywood shear strengths than those made from PCO_2KL without oxidation with substitution of 30% of the PF resin solid using the lignin samples. However, All PCO_2KL-based adhesives showed lower wood failures than those of test samples made from PF resin only. Future research efforts need to focus on understanding the fundamental chemical and physical properties of Kraft lignin and its resins. The search for an economic lignin-based wood adhesive should continue.

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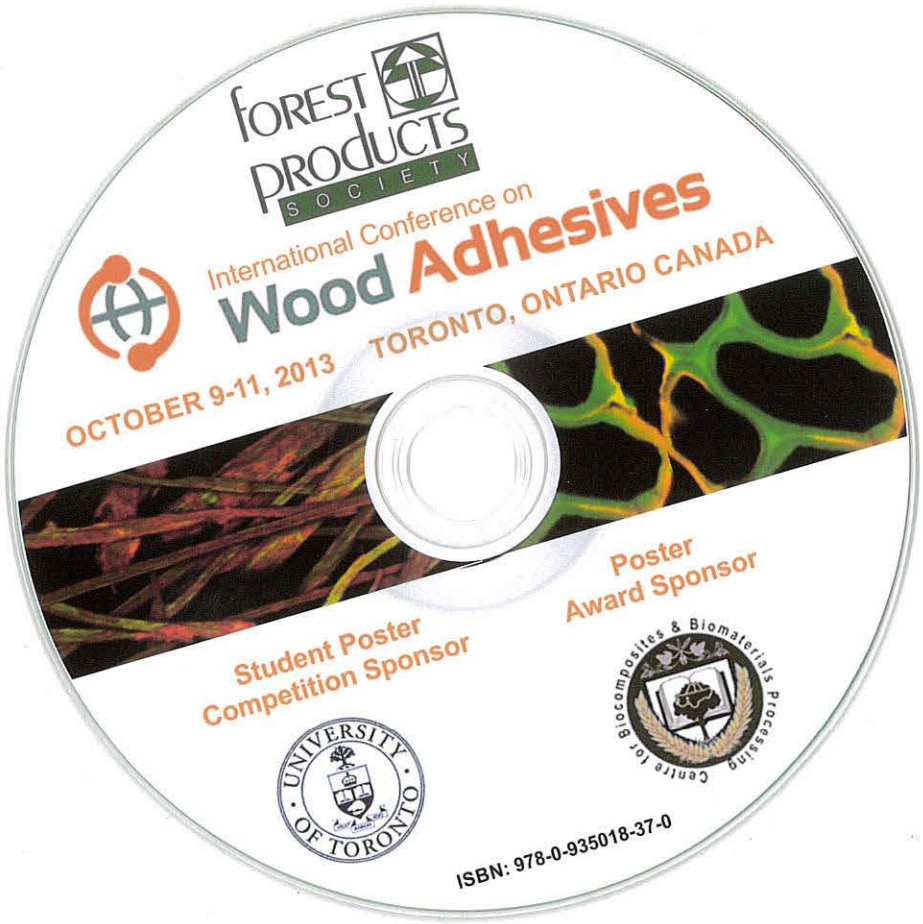
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