Modification of Kraft Lignin for Use as a Replacement for Phenol Formaldehyde in Adhesives

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Abstract

Phenol formaldehyde adhesive is widely used due to its high weather-resistance and water-resistance. Numerous efforts have been carried out to reduce the dependence of this industry on phenol, the cost of which is subject to fluctuations with the price of oil. Several attempts have been made to replace phenol by lignin due to structural similarity and lower cost. Replacement of about 20-25% of the unmodified lignin has been reported in the literature without any significant impact on the properties of the adhesive. Two major problems results in very limited commercial applications of kraft lignin in adhesives. The first being the reactivity of kraft lignin toward formaldehyde is much lower than phenol, resulting in weaker bonds and the second is the high molecular weight and high polydispersity of kraft lignin which causes viscosity problems in resin formulations. Reactivity of kraft lignin towards formaldehyde can be improved by phenolation. Two methods for phenolation were used: a) nucleus exchange reaction was used to produce low molecular lignin compounds, or b) lignin was reacted with a small amount of sulfuric acid in the presence of excess phenol at low temperatures (25-105ºC) for various reaction time. Phenolation of lignin with low dosages of acid was the process of choice due to the lower cost of the reactants involved. Preliminary results with phenolated lignin shows that the modified lignin could be substituted into an adhesive blend at levels up to 35-40% without any effect on dry or wet strength.

Keywords: Lignin, Softwood, Phenolation, Adhesives, Plywood

Introduction

Lignin is the most abundant aromatic natural polymer on earth. Approximately 50 million metric tons of lignin is produced annually as a byproduct of pulp and paper industry. The vast majority of technical lignin produced is kraft lignin. However, up until 2011, only 60,000 tons were produced annually for commercial application. Almost all kraft lignin are currently burned to generate energy and recover cooking chemicals, which is a necessity to render the kraft process economically viable. Nevertheless, about 10-15% of lignin can be extracted from the black liquor without adversely affect the chemical recovery process. The fuel value of kraft lignin in black liquor is currently about $100 per ton. If high value products can be derived from kraft lignin, potentially 5-7.5 million tons could be available from the pulp and paper industry. Currently, approximately 2% of the lignin available from the pulp and paper industry are used commercially [1].

Lignin in nature serves as glue for lignocellulosic materials. There is great interest in using kraft lignin to replace all or a part of phenol formaldehyde (PF) resins due to their similarity in chemical structures and the potential availability in bulk at low cost. Many researchers have investigated the application of kraft lignin as a replacement of phenol formaldehyde resin. With abundant free phenolic hydroxyl groups, kraft lignin has been reported to replace up to 25% of the total amount of phenol formaldehyde resins in the production of plywood [2-4]. Unfortunately, kraft lignin has much lower reactivity towards formaldehyde than phenol, resulting in a very limited commercial application of kraft lignin in PF resins. Another problem of kraft lignin is its higher molecular weight polydispersity, creating viscosity problem in resin formulations. One way to decrease the MW of kraft lignin and to increase its reactivity towards formaldehyde is phenolation. During the past decades, many phenolation studies were carried out. Most studies used a large amount of acid (50% on lignin) in solvents. One of example of previous study is by Funaoka and his colleges which shows that nucleus exchange reaction can depolymerize the lignin and produceguaiacol and catechol [5-6].

Commonly used adhesives includes protein adhesives, animal glues, carbohydrate polymers, natural rubber-based adhesives, elastomeric adhesives, and phenolic resin adhesives. Among those different adhesives, phenol formaldehyde (PF) resins is widely used all over the world because of its good weather and water resistance, and high mechanical strength [7]. The global production of PF was 10.7 million ton in 2012, which is expected to have a production of 18.1 million tons by 2018. PF has broad applications including wood bonding, industrial coatings, construction as well as plywood adhesive. In recent decades, enormous efforts have been carried out to find promising substitution of phenol and reduce the dependence of this industry on petroleum industry. Lignin, due to the similar structure and characterization of sustainability, is one of the promising candidates. Among different lignin resources, such as soda–anthraquinone flax lignin, organosolv lignin, ethanol process lignins, and kraft lignin, researches indicate that kraft lignin is more suitable than others for making lignin based phenol formaldehyde resin since it shows higher reactivity towards formaldehyde [8-9].

In this report, we summarize our ongoing research on phenolation of kraft lignin using low acid charge and its use as an adhesive. Two methods for phenolation were used: a) nucleus exchange reaction was used with BF_3 to produce low molecular lignin compounds, or b) lignin was reacted with a small amount of sulfuric acid in the presence of excess phenol at low temperatures (25-105ºC) for various reaction time.

Materials and Methods

Kraft lignin was obtained from the Domtar mill in Plymouth, North Carolina, which was recovered by the LignoBoost Process and was termed as BioChoice Lignin (BCL). The washed BCL has an ash content of 0.2%, sugar content of 1.7% and lignin content of 97.7%

Boron Trifluoride (BF_3) Catalyzed Reaction of BCL in Phenol

BCL (0.2 g) was dissolve in phenol (2.0 g) at 50ºC in a capped glass centrifuge tube. To the mixture, 0.2 g of phenol/BF_3 reagent (containing 0.01g of BF_3) and the reaction was carried out at a desired temperature for a prescribed period of time as described above in the previous section. After the reaction mixture was cooled down, 30 mL of saturated NaCl solution was used to extract and decompose BF_3. The organic layer was recovered and dissolved in 8 mL of 2 N NaOH, acidified to pH 7 with 2N HCl and extract 3 times with 30 mL of diethyl ether. The aqueous layer is acidified to pH 2.5 with 2 N HCl and the precipitated lignin was filtered, washed and freeze-dried to obtain Phenolated Lignin 1 (PL 1). Ether extractions were combined. A small aliquot was used to determine the recovery of phenol and the formation of guaiacol by gas chromatograph. The rest is evaporated to dryness, dissolved in 10 mL of ether and precipitated into 90 mL of petroleum ether. The precipitated lignin was filtered, washed and recovered as phenolated lignin 2 (PL 2).

Sulfuric Acid Catalyzed Reaction of BCL

BCL (0.2 g) was dissolved in phenol in a capped glass centrifuge tube by heating the mixture to 105ºC with frequent shaking. After the dissolution of BCL, 72% sulfuric acid (10 µL-100 µL) was added and the reaction carried out by placing the centrifuge tube in an aluminum block maintained at the reaction temperature with frequent shaking.

When prescribed reaction time was completed, reaction tube was cool down in an ice/water bath. Subsequently 25 mL of diethyl ether (ether) and 10 mL of D.I. water were added and vigorously mixed and centrifuged. The water layer was removed by Pasteur pipette and another 10 mL of D.I. water was added, mixed and centrifuged. The washing is repeated two more time to remove all acid. After removal of water, the tube contains ether soluble and insoluble fractions. Ether is removed and the insoluble was washed repeatedly (3×) with 10 mL of ether. The ether insoluble is dissolved in 96% aqueous dioxane and freeze-dried to obtain ether insoluble lignin.

The ether extracts were combined and adjusted to 100 mL with ether. One mL aliquot was used to determine guaiacol recovery using gas chromatography. The Other 99 ml of diethyl ether part was evaporated to 10 mL and precipitate into 90 mL of petroleum ether to obtain ether soluble lignin, which was filtered, washed with petroleum ether and freeze-dried in 96% dioxane.

Determination of α-Carbonyl, Phenolic Hydroxyl and Stilbene Contents

The content of α-carbonyl, phenolic hydroxyl and stilbene structures in lignin were measured by UV [10-11]. The stock solution of lignin sample was prepared by dissolving 5 mg of lignin sample in 10 ml of 96% dioxane solution. One mL of the stock solution was diluted to 10 mL with 50% dioxane solution and absorbance of lignin sample at 305 nm measured by a HP8453E UV-VIS spectrophotometer (Hewlett Packard Company, Palo Alto City, CA, USA). In another 10 mL volumetric flask, 1 mL of stock solution was reduced by adding 2 mg of sodium borohydride to the solution and kept at ambient temperature for 24 hours. The reduced lignin solution was acidified with 0.2 N HCl to pH<4 and further diluted to 10 mL with 50% dioxane solution. The reduced spectra of lignin were measured by UV at 305 nm and α-carbonyl content was calculated based on $\Delta\varepsilon_R$ method. The extinction coefficient at 305 nm was 9400 $Lmol^{-1}\ cm^{-1}$.

The reduced solution of lignin samples of 1.0 mL was further ionized with 20 mg sodium hydroxide powder. The different spectra were collected by UV using reduced neutral solution as a reference. The calculations of free phenolic hydroxyl and stilbene moieties were based on the absorbance in ionization difference spectra at 300 nm and 378 nm respectively. The extinction coefficient value for the $\Delta\varepsilon_i$ at 300 nm and 378 nm was 4100 L mol^{-1} cm^{-1} and 24300 Lmol^{-1} cm^{-1}, respectively.

Molecular weight was measured by Gel Permeation Chromatography (GPC)

Molecular weight was measured using gel permeation chromatography (GPC, Shimadzu Prominence Liquid Chromatograph equipped with SPD-20A UV detector) using Styragel Guard (4.6×30 mm), Styragel HR 5E THF (7.8×300 mm) and Styragel HR 1 THF (7.8×300 mm) columns connected in series.

Preparation of PF adhesive

Kraft softwood lignin was acid wash before use in phenolation. Phenol, formaldehyde solution (37%) were purchased from commercial resources. Phenolated lignin were produced using the simplified phenolation procedure, which gave a yield of 130% based on the weight of starting lignin.

The PF adhesive was synthesized by the formulation shown in Table 1. In the first step, phenol, formaldehyde (37%) and NaOH (40%) were mixed in the flask and gradually heated up to 85°C. After 3h reactions, the rest of the NaOH and H_2O were added into the flask and the reactions were continued until the viscosity is around 500 cP.

Table 1. Formulation of PF (F:P=1.9:1)

Component	MW(g)	Purity	Mass	Solids	Moles
Phenol	94.11	1.00	30.0	30.0	0.32
CH_2O	30.03	0.37	49.4	18.3	0.61
40% NaOH-1	40.00	0.40	4.6	1.84	0.046
40% NaOH-2	40.00	0.40	5.2	2.08	0.052
Water	18.00	1.00	10.0		
Total			100.0	52.2	

Preparation of plywood

The adhesive strength of PF, KL-PF and PL-PF bonded plywood were measured according to ASTM D-906(2011). Adhesives were applied to the three-layer poplar plywood (10 in*10 in*1/16 in). The open assembly time was 5 min, and closed assembly time was 15 min for the plywood. The curing conditions for the plywood was 175°C, 125 psi for 5 min. Panels were conditioned at 23°C, 50% RH for 7 days before cutting and testing.

Results and Discussion

Two methods for phenolation were used in this study. The first involves nucleus exchange reaction using BF_3 to produce low molecular lignin compounds and the second uses a small amount of sulfuric acid in the presence of excess phenol at low temperatures.

Phenolation of BCL with BF_3

BCL is dissolved in an excess phenol and phenolation was carried out at 80 and 90^OC for 2 hours by the addition of acid. Yields of ether insoluble lignin (PL 1), ether soluble lignin (PL 2) and guaiacol are shown in Table 1. At high BF_3 dosage, the yields of PL 1 and PL 2 and the total yield were low, indicating formation of some other products from BCL. Furthermore, some guaiacol was formed. At low acid dosage (including sulfuric acid), around 110% of lignin was recovered, indicating condensation of BCL and phenol. No guaiacol was formed as BCL is known to contain 1-2% guaiacol. Without the presence of acid, BCL is recovered almost quantitatively.

Functional groups in BCL, PL 1 and PL 2 produced at two different temperatures with and without acid are given in Table 2. With acid, both PL 1 and PL 2 gave lower contents of α-carbonyl, stilbene and methoxyl group with concomitant increase in the content of free phenolic hydroxyl groups, indicating the condensation of BCL with phenol. Even without the presence of acid, small amount of phenol condensed with lignin as indicated by the small decrease in the contents of α-carbonyl, stilbene and methoxyl group with a small increase in the phenolic hydroxyl content.

Table 1. Yields of Phenolation Reaction Products under Various Conditions for 2 h

Acid % of BCL	Temp. ^OC	Yield PL 1 % of BCL	Yield PL 2 % of BCL	Guaiacol % of BCL	Total yield % of BCL
BF_3 50%	80	59	15	9	83
BF_3 5%	80	79	28	1	108
BF_3 5%	90	66	52	2	110
No acid	80	86	12	1	99
No acid	90	86	10	2	98
H_2SO_4 5%	90	83	27	1	111

Table 2. Functional Groups of BCL and its Phenolation Products

% Acid Temperature	Lignin Sample	α-Carbonyl $/C_9$	Phenolic OH/C_9 %	Stilbene/C_9 %	Methoxyl Wt %
0	BCL	7.8	43	5.8	12.6
50% BF_3 80^OC	PL 1 PL 2	4.7 3.0	70 75	2.4 2.3	8.5 9.1
5% BF_3 80^OC	PL 1 PL 2	5.2 3.9	60 63	1.6 0.8	10.4 3.8
5% BF_3 90^OC	PL 1 PL 2	4.1 1.6	63 66	1.8 1.0	7.7 3.4
0% acid 80^OC	PL 1 PL 2	7.7 4.0	46 52	2.5 2.2	11.8 4.5
0% acid 90^OC	PL 1 PL 2	6.0 2.6	42 50	2.5 2.0	8.7 4.4
5% H_2SO_4 90^OC	PL 1 PL 2	2.9 2.5	53 78	1.5 1.3	10.1 8.0

Gel permeation chromatograms of PL 1 and PL 2 produced with and without BF_3 are shown in Figures 1 and 2, respectively. In the presence of 5% BF_3, PL 1 and PL 2 have much lower molecular weight (MW) and narrower MW distribution than the original BCL (Fig. 1), indicating degradation of BCL in addition to the condensation of phenol during the phenolation reaction. Similar results were observed in reaction of BCL with sulfuric acid in guaiacol. Without acid, no degradation of BCL occurs albeit some condensation of phenol to lignin as discussed above.

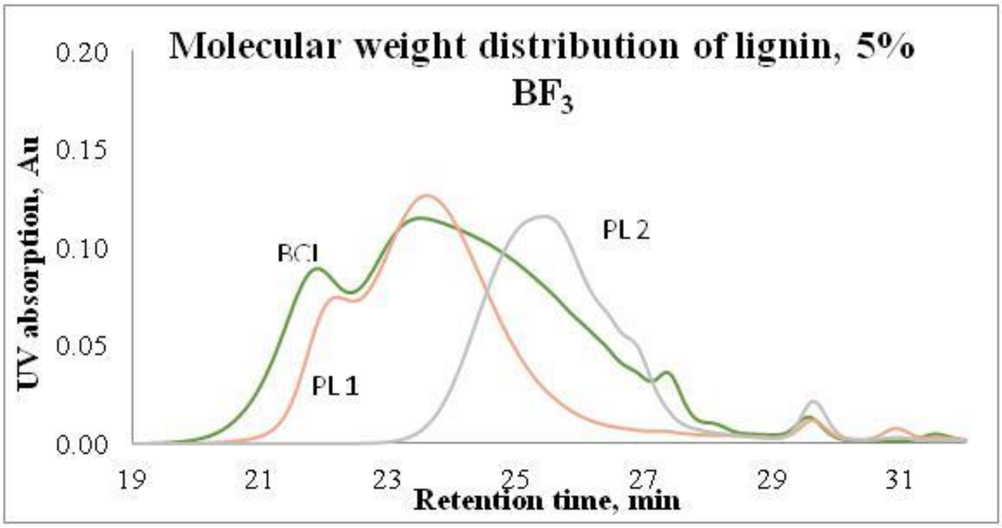


Figure 1. GPC of PL1 and PL2 Produced at 90^{O}C with 5% BF_3 for 2 h

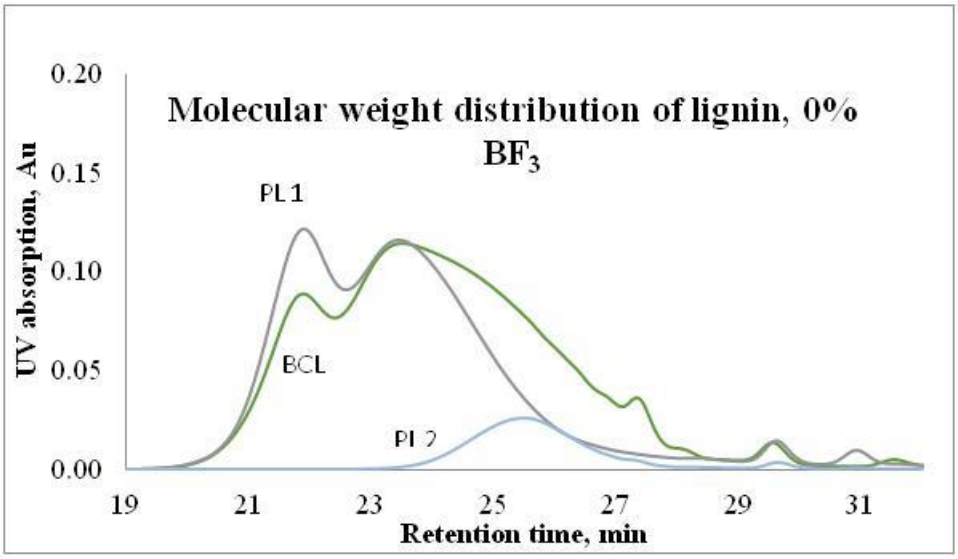


Figure 2. GPC of PL 1 and PL 2 Produced at 90^{O}C Without BF_3 for 2 h

Reaction of BCL Catalyzed by Sulfuric Acid in the Presence of Phenol

The material balance of BCL reacted with phenol in the presence of different amounts of sulfuric acid is shown in Table 3. As can be seen, quantitative recovery of lignin is achieved with 77-81% of ether insoluble and 21-27% of ether soluble.

Contents of α-carbonyl, phenolic hydroxyl and stilbene structures in the reaction products are shown in Table 4. Compared with corresponding structures in BCL, α-carbonyl and stilbene structures decrease and phenolic hydroxyl content increase substantially, suggesting that guaiacol are adding on to BCL. The large increase in the phenolic hydroxyl content cannot be explained by the addition of phenol to the α-carbonyl and stilbene structures alone. Acid catalyzed degradation of BCL must also occur, as GPC clearly shows lower molecular weight of both ether insoluble and ether soluble lignin. Optimum conditions to obtain phenolated lignin with high phenolic hydroxyl content, lower α-carbonyl and stilbene contents and lower molecular weight of both ether insoluble and ether soluble lignin was found to be at 105^{O}C with 10% sulfuric acid dosage for 0.5 hour. Extend reaction time beyond 0.5 hour or increase acid dosages gave little improvement. The molecular weight distribution of the original lignin (BCL) and the ether soluble (PL2) and ether insoluble (PL1) fractions are shown in Figure 3.

Table 3. Material Balance of Reacted BCL at 105 and 80°C with Sulfuric Acid

	H_2SO_4 (% on lignin)	5	5	10	20
	Reaction time (h)	0.5	2	0.5	0.5
80 °C	PL1 Ether Insoluble (%)	78.8	77.2	80.3	80.8
	PL 2 Ether Soluble (%)	20.7	25.2	20.5	22.8
	Sum (%)	99.5	102.4	100.8	103.6
105°C	PL1 Ether Insoluble (%)	-	-	77.3	-
	PL2 Ether Soluble (%)	-	-	26.8	-
	Sum (%)	-	-	104.1	-

Table 4. Contents of Functional Groups in Reaction Products

Reaction temp.	80 °C									105 °C	
Sample type	BCL	PL1 Ether Insoluble				PL2 Ether Soluble				Ether Insul.	Ether Soluble
H_2SO_4 (% of BCL)		5	5	10	20	5	5	10	20	10	10
Reaction time (h)		0.5	2	0.5	0.5	0.5	2	0.5	0.5	0.5	0.5
[α-carb.]/[C9] (%)	8.7	6.7	6.6	4.9	4.4	8.4	6.1	7.9	6.1	4.8	4.6
[ph-OH]/[C9] (%)	44	57	59	57	66	63	80	68	73	63	77
[stilbene]/[C9] (%)	4.8	2.2	2.7	2.3	2.0	5.6	2.7	5.2	3.4	2.2	3.3

Contents of α-carbonyl, phenolic hydroxyl and stilbene structures in the reaction products are shown in Table 4. Compared with corresponding structures in BCL, α-carbonyl and stilbene structures decrease and phenolic hydroxyl content increase substantially, suggesting that guaiaicol are adding on to BCL. The large increase in the phenolic hydroxyl content cannot be explained by the addition of phenol to the α-carbonyl and stilbene structures alone. Acid catalyzed degradation of BCL must also occur, as GPC clearly shows lower molecular weight of both ether insoluble and ether soluble lignin. Optimum conditions to obtain phenolated lignin with high phenolic hydroxyl content, lower α-carbonyl and stilbene contents and lower molecular weight of both ether insoluble and ether soluble lignin was found to be at 105°C with 10% sulfuric acid dosage for 0.5 hour. Extend reaction time beyond 0.5 hour or increase acid dosages gave little improvement. The molecular weight distribution of the original lignin (BCL) and the ether soluble (PL2) and ether insoluble (PL1) fractions are shown in Figure 3.

Process Optimization

Phenolation of kraft lignin with excess phenols in the presence of catalytic amount of acid (BF_3 or H_2SO_4) occurs at 60-100 ^{O}C, with degradation of ether linkages in lignin, resulting in lower molecular weight and lower dispersity. Condensation of phenol with α-hydroxy/-ether, addition of phenol to α-carbonyl, stilbene and vinyl ether structure occurs. No nucleus exchange reaction occurs at low acid dosage and low temperatures. In both cases substantial increase of phenolic hydroxyl content of modified lignin occurs which should be beneficial for adhesive applications.

Even though reacting with BF_3 produces phenolated lignin it was seen as too expensive for commercialization. The reaction with low dosages of sulfuric acid has a higher potential for commercialization due to the low cost of the chemicals. The sulfuric acid catalyzed reaction system was simplified in order to evaluate its potential for commercialization. The simplified process is shown in Figure 4. The reacted lignin is not separated into two fractions. The properties of the phenolated lignin using this simplified procedure are shown in Table 5. Based on optimization studies the recommended reaction conditions are 5% sulfuric acid and a 5:3 phenol to lignin ratio.

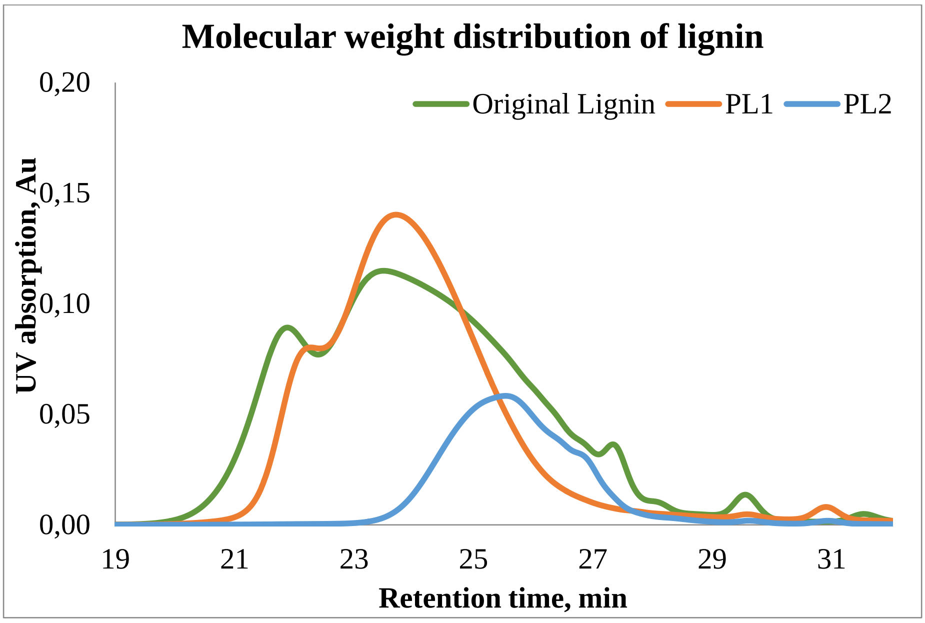


Figure 3. GPC of PL1 and PL2 Produced at 90^{O}C with 5% Sulfuric Acid

Table 5. Properties of the Phenolated Lignin Using Simplified Procedure

Sample	α-carbonyl %C_9	ph-OH %C9	Stilbene %C9	Mn, g/mol	Mw, g/mol	Mw/Mn
BCL	15.8	45.3	3.5	969	8852	7.0
BCL/5% H2SO4	3.9	57.9	1.1	1209	4130	2.6

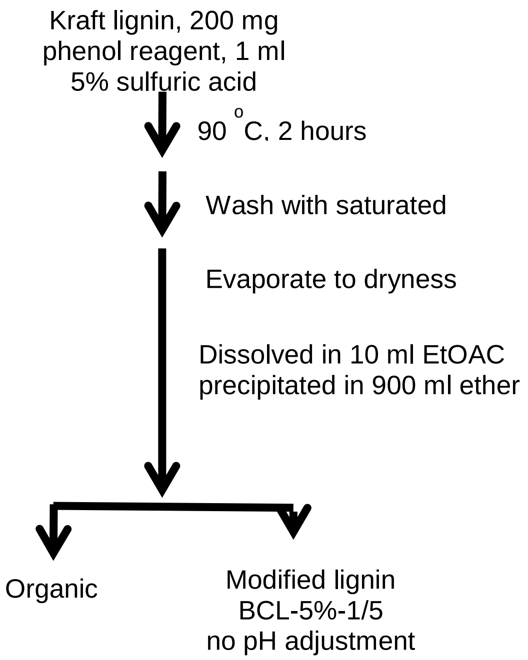
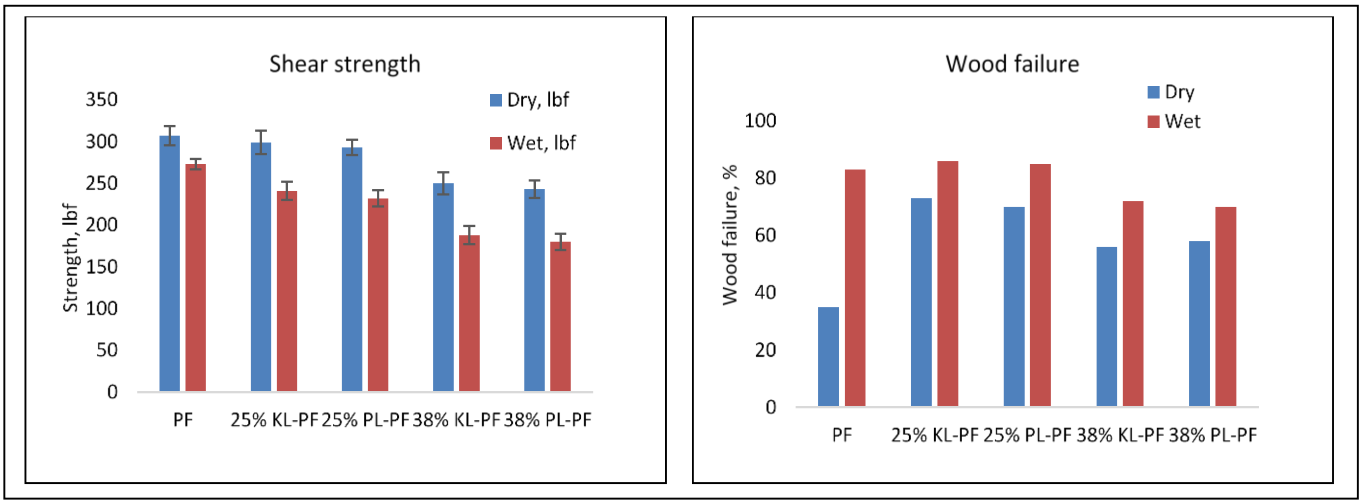


Figure 4. Simplified Procedure for Lignin Phenolation using Sulfuric Acid

Adhesive Testing of KL-PF and PL-PF

Figure 5 show the shear strength and wood failure of PF and LPF. As these figures shown, KL-PF and PL-PF show no big difference in shear strength and wood failure for both 25% and 38% substitution rate. Up to 25% substitution rate can be achieved without significant sacrifice of the shear strength, but with higher wood failure. Although UV-Vis data indicates that phenolated lignin has higher phenolic hydroxyl group content than technical lignin, PL-PF in this case shows comparative results with KL-PF. The limited formaldehyde amount may be the reason. In the experiment, formaldehyde amount was controlled the same with KL-PF and PL-PF, so although PL has more reactive sites and higher reactivity than KL, some sites were unreacted, which leads to the limited performance of PL-LPF. Lignin based phenol formaldehyde adhesives (LPF) as 50% substitution rate cannot be made under the reaction conditions. Both 50% KL-PF and 50% PL-PF gelled during reactions.

Figure 5. Shear Strength and Wood Failure Rates of PF and LPF adhesives



Adjustment of formaldehyde for PL-PF

In order to prove the hypothesis that the performance of PL-PF is limited by the amount of formaldehyde, formaldehyde amount was adjusted based on the reactivity. In this case, formaldehyde to free phenol was kept at 1.9, and formaldehyde to attached phenol on lignin was kept at 1. Table 6 shows the different components used. Their performances were compared with unadjusted formulations.

Table 6. Comparison of Formulations for Adjusted and Unadjusted LPF

	Phenol, g	CH_2O (37%), g	PL, g	
			Lignin	Attached phenol
PF	30	49.4	0.0	0.0
25% PL-PF	22.5	36.9	7.5	2.2
25% PL-PF-a[1]	22.5	38.8	7.5	2.2
38% PL-PF	18.6	30.5	11.4	3.4
38% PL-PF-a	18.6	33.5	11.4	3.4

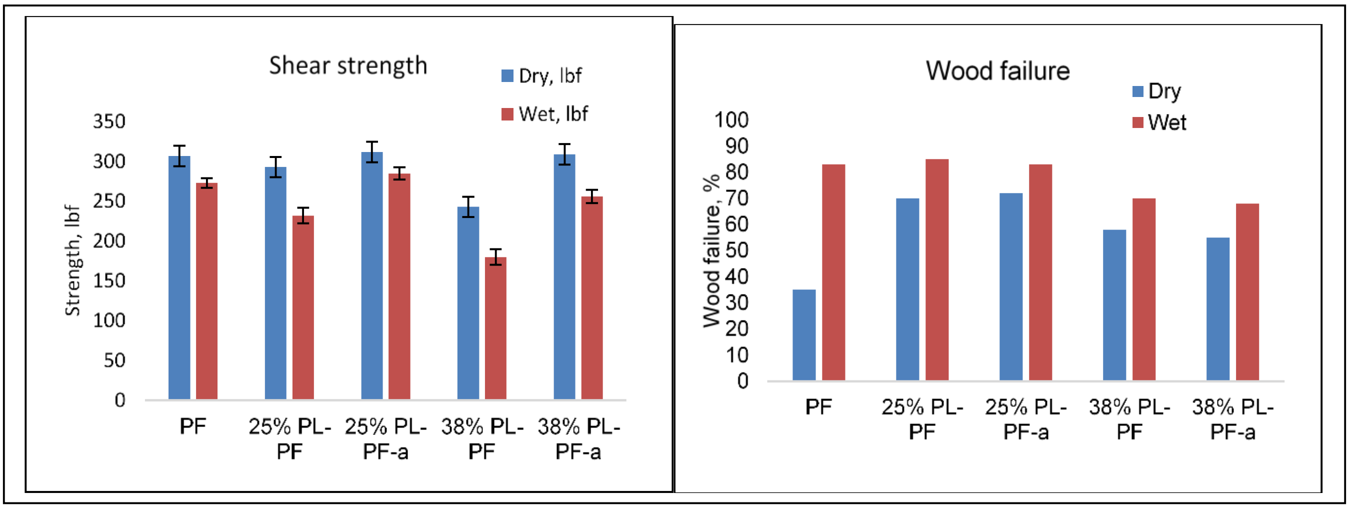


Figure 6, Shear Strength and Wood Failure Rates of PF and LPF adhesives

1: PL-PF-a is adjusted PL-PF resin

Effects of formaldehyde adjustment on shear strength for PL-PF

As shown in Figure 3 and 4, after the adjustment of formaldehyde amount, shear strength of PL-PF increases at both 25% and 38% substitution rate. Wood failure keeps comparable level with unadjusted ones. On the other hand, with phenolated lignin, up to 38% of modified phenolated lignin can be achieved without sacrificing of physical properties.

Conclusions

BCL may be activated for adhesive application by dissolving BCL in excess phenol and reacted at 90°C with 5% of acid (BF_3 or H_2SO_4). The resulting phenolated BCL has lower MW and narrower MW distribution and presumably high reactivity than the original BCL. With unmodified technical kraft softwood lignin, up to 25% of substitution rate can be achieved without significant sacrifice of shear strength, and with higher wood failure. For better utilization of modified phenolated lignin, formaldehyde amount need to be adjusted based on reactivity for different substitution rate. After adjustment, up to 38% of phenol can be replaced with phenolated lignin with comparable shear strength.

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