Evaluation of Phenol-Formaldehyde Resins Modified and Blended with Pyrolysis Bio-Oil for Plywood

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Abstract

The objective of this study was to compare the characteristics and bonding performance of phenol-formaldehyde (PF) resins modified and blended with crude bio-oil. For modified PF resins, crude bio-oil from the pyrolysis of pinewood was synthesized with phenol and formaldehyde at 10, 25, 50, and 75 percent phenol substitution percentages, respectively. For blended PF resins, crude bio-oil was physically blended with PF resin at 4, 13, 23, and 38 percent addition percentages, respectively. The physical properties of crude bio-oil and PF resins, such as viscosity, pH value, gel time, water content, and solid content, were measured. The bond strength of plywood was evaluated. The results indicated that incorporating crude bio-oil into PF resin either by synthesis or by blending at certain amounts could improve the bonding performance of PF resins. For blended PF resins, the best crude bio-oil addition percentage was 13 percent, while for synthesized (modified) PF resins, the best phenol substitution percentage was 25 percent. Further increment of the crude bio-oil content level decreased the bond performance of both modified and blended PF resins. This was mainly due to the increased viscosity and the acidity of blended PF resins at a high crude bio-oil addition percentage and a shortage of reactive phenolic compounds in modified PF resins at a high phenol substitution percentage. Plywood bonded with the resins could generally meet the requirement of Chinese National Standard GB/T 17657-2013 and be suitable for outdoor applications.

As a typical type of phenolic resin, phenol-formaldehyde (PF) resin, has been widely used in the wood panel industry, especially for outdoor applications, because of its good bonding performance and high durability (Gardziella et al. 2000). However, one of its starting chemicals, phenol, is derived from petroleum, which means it is nonrenewable and its price and availability strongly depend on fossil fuels. Pyrolysis of woody biomass produces a liquid product called bio-oil (Mohan et al. 2006). Bio-oil has a typical water content of 15 to 30 percent (Zhang et al. 2007). Besides water, there are other compounds in the bio-oil, such as sugars, alcohols, aldehydes, ketones, organic acids, and phenolic compounds with various molecular weights (Mohan et al. 2006). Phenolic compounds in bio-oil are phenol and its oligomers with various numbers of phenolic rings (Kim 2015). Therefore, bio-oil is expected to be a potential source for energy and chemical supply in the future (Mao et al. 2011, Celikbag and Via 2015). In particular, phenolic compounds in bio-oil have various uses in resin industry, e.g., as alternative chemicals for phenolic resins.

In the past decade, biomass-derived phenolic compounds have been used in PF resins, in which two major approaches have been applied (Mao et al. 2017). The first approach is to replace commercial phenol in synthesis of phenolic resins (Chaouch et al. 2014), and the second is to blend commercial PF resin with bio-oil to make resin blends (Aslan et al. 2015). Compared with the first approach, the second approach seems to have the simplest operating procedure. However, attention should be paid to high acidity and viscosity of bio-oil. These two parameters might result in resin blends with abnormal pH value and viscosity, both of which are important resin application parameters (Mao et

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al. 2017). In both approaches, bio-oil could be either simply applied without further processing (crude bio-oil from pyrolysis; Chan et al. 2002, Chaouch et al. 2014) or processed and treated (phenol-rich fraction) before being applied (Sukhbaatar et al. 2009). Nevertheless, directly using untreated crude bio-oil should be a relatively economical way of application, and the aldehydes in bio-oil also have the potential for partial replacement of formaldehyde used in the synthesis of PF resins (Choi et al. 2015). However, the mixture of phenolic compounds is complex, and the percentage of real reactive phenolic compounds in raw bio-oil is low (Aslan et al. 2015). Therefore, usually, bio-oil is treated to obtain a higher percentage of reactive phenolic compounds for resin synthesis. The processing approach of bio-oil includes pretreatment of biomass feedstock (or use of feedstock with high lignin content) (Lu et al. 2013), modification of pyrolysis condition (such as catalytic pyrolysis; Yoshikawa et al. 2013), and postprocessing of bio-oil (such as hydrogenation, hydrodeoxygenation, catalytic cracking, steam reforming, molecular distillation, esterification, emulsification, and solvent extraction of bio-oil; Dobele et al. 2010, Aslan et al. 2015, Ozbay and Ayrilmis 2015). These methods may finally result in PF resins with better performance but also higher production costs.

Although the application of bio-oil in PF resin was actively studied in recent years, limited reports were found on comparing PF resins made from these two utilization approaches. Resins obtained from these two methods would have different structures, curing behaviors, application performances, and even costs, which would undoubtedly result in panels with varied properties. The objective of this study was to compare the characteristics and performance of PF resins synthesized and blended with crude bio-oil, respectively. The goal of the research was to develop a performance competitive bio-based PF resin with reasonable cost and easy operation procedure for the wood engineering panel industry.

Materials and Methods

Materials

Phenol (99%), formaldehyde (37%), and sodium hydroxide (NaOH) were obtained from a local resin manufacturing factory. Pinewood (Chinese pine) chips were harvested from a local forest management area. These pine trees were 6 years old. These pinewood chips, mixed with a small fraction (about 10%) of bark, were ground and sieved to a particle size of 16 to 20 mesh and dried for 12 hours at 103°C prior to the pyrolysis. Poplar veneers with a thickness of 1.5 to 1.6 mm and moisture content of 8 to 10 percent were obtained from a local plywood factory.

Bio-oil production

Bio-oil was produced from the pyrolysis of pinewood in a fluidized-bed reactor. Nitrogen was used at a flow rate of 100 to 150 cm^3/min to exclude oxygen from the system at the feed hopper. The particles were pyrolyzed at 450°C under atmospheric pressure with a retention time of 2 seconds. The crude bio-oil was filtered by a charcoal filter to remove solid residuals and then stored in sealed glass bottles in the dark at 4°C to 5°C.

Bio-oil physical properties

The bio-oil water content was measured by the Karl Fisher titration method with an HI 903 Karl Fischer Volumetric Titration apparatus (Hanna Instruments Inc., Woonsocket, Rhode Island) (Mohan et al. 2006). The viscosity was measured at 25°C in accordance with Chinese National Standard GB/T 14074-2006 (Standardization Administration of the People's Republic of China [SAC] 2006) with a rotational DVS+ viscometer (Brookfield Engineering Laboratories, Inc., Middleboro, Massachusetts). The pH value was measured at 25°C in accordance with Chinese National Standard GB/T 14074-2006 with a digital pH meter (EUTECH PH5+, Waltham, Massachusetts). Three replicates were performed for each test.

Gas chromatography–mass spectrometry (GC-MS) analysis of bio-oil

The test procedure followed that described in a previous publication (Li et al. 2013). The chemical composition of bio-oil was analyzed utilizing a 5890 series II gas chromatograph equipped with a 5971 series mass spectrometer (Hewlett-Packard, Santa Clara, California). The injector temperature was 280°C. A ZB-5 capillary column (30-m by 0.32-mm inner diameter × 0.25-μm film thickness) was used at an initial 40°C (held for 4 minutes), followed by heating at 5°C/min to a final temperature 280°C and held for 15 minutes. The mass spectrometer employed a 70-eV electron impact ionization mode, a detector temperature of 260°C, and an interface temperature of 270°C. The carrier gas was He (99.99% purity), and the flow rate was 1 mL/min. The ratio of mass to charge (m/z) value (the fragment ion of the compound) was recorded for each compound.

Resin preparation

Control PF resin, with a molar ratio of formaldehyde to phenol (F/P) of 2.0, was synthesized using a conventional procedure with phenol (P) charged once and formaldehyde charged twice (F_1 and F_2; Pocius 2002). NaOH (40%) was divided into two portions (S_1 and S_2) and charged with F_1 and F_2, respectively. At the beginning, the calculated amounts of P (376.0 g), F_1 (389.2 g), and S_1 (43.7 g) were charged into a four-neck round-bottom flask equipped with a mechanical stirrer and a reflux condenser. The reaction mixture was heated to 90°C and maintained for 45 minutes under stirring. Then the mixture was cooled to 70°C. F_2 (259.5 g) and S_2 (29.2 g) were charged into the flask. The mixture was heated to 85°C and kept at this temperature until the viscosity of the resin reached 350 to 400 cP. The synthesized control PF resin was marked as PF-C (Table 1).

The modified PF resins were synthesized with phenol partially replaced by bio-oil at various percentages (10%, 25%, 50%, and 75%, based on the weight of phenol). The synthesis procedure was similar to that of control PF resin. Bio-oil was charged together with the phenol. The synthesized modified PF resins were marked as PF-M-10, PF-M-25, PF-M-50, and PF-M-75, respectively (Table 1).

The blended PF resins were prepared by physically blending control PF resin with bio-oil at various percentages (4%, 13%, 23%, and 38%, based on the weight of control PF resin). The blended PF resins were marked as PF-B-4, PF-B-13, PF-B-23, and PF-B-38, respectively (Table 1). Here it needs to be noted that these percentages were specially chosen to ensure the same amount of bio-oil contents in

Table 1.—*Resin preparation.*[a]

PF resin	Resin code	Phenol substitution percentage (based on the weight of phenol)	Bio-oil addition percentage (based on the weight of PF resin)
Control	PF-C	0	0
Modified	PF-M-10	10	—
	PF-M-25	25	—
	PF-M-50	50	—
	PF-M-75	75	—
Blended	PF-B-4	—	4
	PF-B-13	—	13
	PF-B-23	—	23
	PF-B-38	—	38

[a] PF = phenol-formaldehyde.

modified and blended PF resins with equal weights. For example, 100 g of PF-M-10 resin and PF-B-4 resin contained the same amounts of bio-oil. In this way, the comparison study would be more meaningful and convincing.

Resin properties evaluation

The pH of the resins was measured at 25°C in accordance with Chinese National Standard GB/T 14074-2006 (SAC 2006) using the EUTECH PH5+ pH meter. The viscosities of the resins were measured at 25°C in accordance with Chinese National Standard GB/T 14074-2006 with a rotational Brookfield DVS+ viscometer. The gel times of the resins were measured at 100°C (boiling water) in accordance with Chinese National Standard GB/T 14074-2006. The solid contents of the resins were measured by oven-drying the resin sample at 125°C for 2 hours. Three replicates were performed for each test.

Panel manufacturing

Three pieces of veneers with a density of about 0.382 g/cm^3 for the plywood top, middle, and bottom layers were cut in an end-match manner for plywood manufacturing to minimize the impact of wood variation on final panel performance. The plywood with dimensions of 300 by 300 mm was manufactured using a laboratory hot press. The resin application rate was 280 g/m^2 (double glue line). The resins were applied uniformly on both sides of the middle veneer and the loose side of the top- and bottom-layer veneers, respectively. The hot press time, temperature, and pressure were 5 minutes, 135°C, and 1.0 to 1.2 MPa, respectively. Two panels were made for each resin formulation. After pressing, the plywood panels were conditioned at 20°C and 60 percent relative humidity for 1 week.

Measurement of the bonding strength

The bonding strength was measured according to Chinese National Standard GB/T 17657-2013 (SAC 2013). Six specimens with dimensions of 100 by 25 mm were cut from each panel to make a total of 12 specimens for each resin formulation. Among them, six specimens were randomly selected and tested for dry strength, and the remaining six specimens were tested for wet strength. Before the testing of wet strength, specimens were immersed in boiling water for 4 hours, dried in an oven at 63°C for 18 hours, and then immersed in boiling water again for 4 hours. After the water-immersion treatment, the specimens were cooled down in water at 25°C and tested by lap shear strength in an MTS universal testing machine (MTS Systems Corporation, Eden Prairie, Minnesota).

Results and Discussion

Bio-oil physical properties

Water content, pH, and viscosity of bio-oil are summarized in Table 2. The pH value of crude bio-oil is 2.6, similar to other reported values of crude bio-oil from pinewood (Mohan et al. 2006, Pittman et al. 2012). The low pH of bio-oil could be attributed to the carboxylic acids (such as acetic acid) contained in the bio-oil (see GC-MC results in Table 3). The viscosity of the bio-oil is 1,468 cP. The relatively high viscosity could be attributed to the presence of high-molecular-weight compounds, such as the pyrolyzed lignin fraction in the bio-oil; to a relatively low water content; and to the dragging effect between side chains attached on the bio-oil molecules (Shahid et al. 2014). The water content of the bio-oil is 20.5 percent. The water in the bio-oil was derived from the original moisture in the biomass feedstock and the product of dehydration during the pyrolysis process and storage (Zhang et al. 2007). Water content is an important parameter of bio-oil because it could affect viscosity, flowability, storage stability, and chemical reactivity. In some applications, water needs to be taken off; however, this may result in bio-oil with extremely high viscosity.

Chemical composition of bio-oil

Figure 1 shows the GC-MS chromatogram of the bio-oil. According to the results of GC-MS analysis, 22 volatile and semivolatile compounds were identified and quantified in the bio-oil (Table 3). These compounds are only a fraction of the total organic chemical components in the bio-oil (Li et al. 2013, Aslan et al. 2015). Wood is composed of cellulose, hemicellulose, and lignin. The degradation of cellulose and hemicellulose produces acids, anhydrosugars, aldehydes, alcohols, and ketones of small molecular weight. These compounds may have less contribution to PF resin and wood bonding (Aslan et al. 2015). The degradation products of lignin include mainly a series of phenolic compounds, such as phenol, methylphenols, methoxyphenols, ethylphenols, propylphenols, and benzenediols (Mohan et al. 2006, Bu et al. 2011). These phenols and phenolic compounds were also identified in this study. They are important reactive components in PF reactions and could also be useful chemicals in other industries (Bu et al. 2013).

Resin physical properties

Viscosity, gel time, solid content, and pH value results of modified and blended PF resins are presented in Table 4. For the blended PF resins (PF-B resins), the viscosity increased with bio-oil content (from 378 cP for resin PF-C to 599 cP for resin PF-B-38), while for the modified PF resins (PF-M resins), the viscosities were in the range of 334 to 367 cP, similar to that of the control PF resin. The viscosities of PF-M resins could be readily adjusted during resin synthesis to comply with the requirement of specific applications, such as for plywood or for particleboard and oriented strand board. However, the viscosities of PF-B resins were closely related to the amount of crude bio-oil in resin blends (Aslan et al. 2015). As the amount of bio-oil in resin blends

Table 2.—Physical properties of the bio-oil.

Property	Value (SD)
Viscosity (cP)	1,468 (20)
pH	2.6 (0.05)
Water content (%)	20.5 (0.6)

increased, less of water was brought in, resulting in higher solid contents of resin blends. The viscosities would increase accordingly. According to the results (Table 4), the viscosities of blended PF resins might still be suitable for bonding plywood and laminated veneer lumber but might be too high for particleboard and oriented strand board applications.

The solid content of control PF resin was 48.7 percent. The solid contents of PF-M and PF-B resins ranged from 43.7 to 47.5 percent and from 48.6 to 56.7 percent, respectively. The decrease of solid content of PF-M resins with increasing substitution percentage of phenol could be attributed to the high water content of bio-oil (20.5%) compared with that of phenol substituted ($\leq$1%), while the increase of solid content of PF-B resins with increasing bio-oil addition percentage could be attributed to the low water content of bio-oil compared with that of control PF resin ($\leq$51.3%).

The pH value of control PF resin was 12.3. As the bio-oil addition increased from 4 to 38 percent, the pH of the PF-B resins decreased from 11.7 to 9.5. The decrease of the pH should be attributed mainly to the organic acids (carboxylic acids) in the bio-oil. Therefore, more alkaline might be needed for PF-B resins due to high acidity of the bio-oil (pH 2.6). As the phenol substitution increased from 10 to 75 percent, the pH of the PF-M resins also decreased but in a minor way. The reason may be that during the synthesis of PF-M resins, the carboxylic acids in the bio-oil were partly neutralized by the alkaline added at the beginning of the resin synthesis.

For the PF-B resins, with the increasing of bio-oil addition percentage, the gel time decreased first and then increased quickly. The decrease in gel time might be owing to the increase in molecular weight of the blended resins, as it is generally believed that resins of high molecular weight cure in less time because of the lower activation energy needed (Aslan et al. 2015). Moreover, some chemicals in the bio-oil, such as phenolic compounds, might serve as cross-linking agents to promote gelling (Hu et al. 2013). As the addition percentage exceeded 13 percent, the increase in gel time might be attributed to the low polymerization reactivity of the PF-B resins and also decreasing pH values. For the PF-M resins, the trend was similar. The decrease in gel time might be because of the increased F/P molar ratio at the lower bio-oil addition percentage. As the addition percentage exceeded 50 percent, PF-M resins have a gel time higher than control PF resin, suggesting the low reactivity of bio-oil compared with phenol owing to fewer free positions in the aromatic rings or an excess of formaldehyde.

Panel bonding performance

The bond strength and wood failure percentage of the control PF resin and modified and blended PF resins were determined (Table 5). Both dry and wet strengths of control PF resin could meet the requirements of Standard GB/T 17657-2013 (SAC 2013) for outdoor applications ($\geq$1.0 MPa for dry strength and $\geq$0.7 MPa for wet strength).

The dry bond strength of PF-M resin increased first with phenol substitution percentage (up to 25%) and then decreased significantly. The dry bond strength is affected by the homogeneity and fluidity of the resins (Jin et al. 2010). For the PF-M resins, bio-oil could react with resin chemicals to obtain clear, dark brown resin liquid with high homogeneity. The viscosity of resins could also be controlled well during synthesis to make resin with good

Table 3.—Chemical composition of the bio-oil.

| Compound		Target quantitation results			
No.	Name	Retention time (s)	Quantitation ion	Concentration in bio-oil (wt%)	Category
1	Acetic acid	2.81	43	5.65	Acid
2	Furfural	10.11	96	0.10	Aldehyde
3	2-Methyl-2-cyclopenten-1-one	13.16	96	0.08	Ketone
4	3-Methyl-2-cyclopenten-1-one	15.82	96	0.05	Ketone
5	Phenol	16.22	94	0.11	Phenol
6	3-Methyl-1,2-cyclopentanedione	18.31	112	0.34	Ketone
7	2-Methylphenol	19.45	108	0.05	Phenol
8	3-Methylphenol	20.32	108	0.07	Phenol
9	2-Methoxyphenol	20.90	124	0.48	Phenol
10	2,4-Dimethylphenol	23.32	122	0.05	Phenol
11	3-Ethylphenol	23.86	122	0.04	Phenol
12	2,3-Dimethylphenol	24.27	122	0.03	Phenol
13	1,2-Benzendiol	24.85	110	0.27	Phenol
14	5-(Hydroxymethyl)-2-furaldehyde	26.12	97	0.37	Aldehyde
15	3-Methyl-1,2-benzenediol	27.25	124	0.09	Phenol
16	4-Ethyl-2-methoxy-phenol	28.03	137	0.27	Phenol
17	4-Methyl-1,2-benzenediol	28.37	124	0.28	Phenol
18	Eugenol	30.78	164	0.15	Phenol
19	2-Methoxy-4-propylphenol	31.11	137	0.07	Phenol
20	Vanillin	32.24	151	0.35	Aldehyde
21	2-Methoxy-4-(1-propenyl) phenol	33.92	164	0.83	Phenol
22	Oleic acid	52.43	55	0.74	Acid

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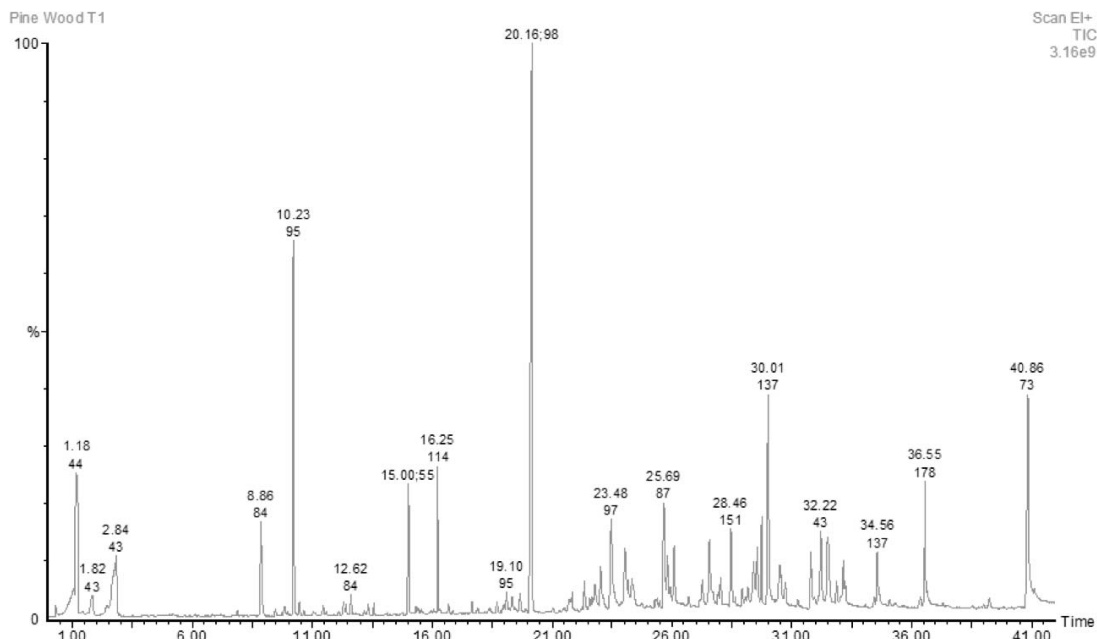
Figure 1.—Gas chromatography–mass spectrometry chromatogram of bio-oil.

fluidity. Therefore, even with a bio-oil substitution amount of 50 percent, the PF-M resin still had appropriate viscosity and could be spread well on the veneer surface. These could contribute to good dry bond strength.

However, when the phenol substitution was 75 percent, the dry bond strength and wood failure percentage became much lower, indicating that too high a substitution percentage was used. This might be attributed to a less cross-linked PF resin structure because of the shortage of phenol.

The trend was similar for PF-B resins, but the dry bond strength reached the highest value at a phenol substitution of 13 percent, after which it started to decrease significantly. Phenolic compounds in the bio-oil might serve as cross-linking agents to improve resin curing (Hu et al. 2013). However, with the increasing bio-oil addition percentage (from 4% to 38%), the viscosity of PF-B resin increased quickly from 418 to 599 cP (Table 4). High viscosity would affect the wettability of resin to the veneer surface, the spreading of resin on the wood surface, and also the penetration of resin into the wood, which are important factors for the formation of good dry strength for wood bonds.

Statistical analysis also showed that at a lower bio-oil content level, for the same bio-oil amount (e.g., PF-M-10 resin and PF-B-4 resin), the dry bond strength of PF-M resin was about the same as that of PF-B resin. At a higher bio-oil content level, for the same bio-oil amount (e.g., PF-M-25 resin and PF-B-13 resin), the dry bond strength of PF-M resin was significantly higher than that of PF-B resin. However, further increasing the bio-oil amount to 50 or 75 resulted in the same dry bond strength for PF-M and PF-B resin. Further research is needed to explain these data.

With the increasing phenol substitution percentage, the wet bond strength of PF-M resins did not increase significantly at a substitution percentage of 25 percent; however, it decreased significantly at a substitution percentage of 50 and 75 percent. At a substitution percentage of 25 percent, the wet strength reached the highest value (1.75 MPa). The possible reason should be that the substitution of part of the phenol with the bio-oil would increase the final F/P molar ratio of PF resins, resulting in a higher cross-linking network of cured resin with better water resistance. However, with the increasing of substitution percentage, more phenol was substituted by bio-oil. The phenolic compounds in bio-oil are less reactive

Table 4.—Physical properties of the resins.[a]

Resin code	Viscosity (cP)	pH	Solid content (wt%)	Gel time (s)
PF-C	378 (3.1)	12.3 (0.04)	48.7 (0.22)	379 (15)
PF-M-10	332 (5.0)	11.4 (0.05)	47.5 (0.14)	355 (18)
PF-M-25	334 (3.2)	10.2 (0.05)	46.5 (0.18)	376 (27)
PF-M-50	327 (4.3)	10.3 (0.06)	45.3 (0.20)	441 (33)
PF-M-75	367 (6.0)	10.7 (0.08)	43.7 (0.11)	638 (31)
PF-B-4	418 (2.2)	11.7 (0.12)	48.6 (0.23)	370 (21)
PF-B-13	465 (2.3)	11.3 (0.21)	50.6 (0.16)	333 (29)
PF-B-23	512 (3.2)	10.7 (0.25)	53.8 (0.18)	406 (24)
PF-B-38	599 (7.1)	9.5 (0.36)	56.7 (0.29)	482 (23)

[a] Standard deviations are presented in parentheses. PF = phenol-formaldehyde.

Table 5.—Bonding performance of the panels.[a]

Resin code	Dry strength (MPa)	Wood failure (%)	Wet strength (MPa)	Wood failure (%)
PF-C	1.52 (0.13) C	100	1.47 (0.04) B	90
PF-M-10	1.84 (0.16) B	100	1.67 (0.09) A	90
PF-M-25	2.09 (0.27) A	90	1.75 (0.11) A	80
PF-M-50	1.58 (0.12) C	80	0.87 (0.10) C	80
PF-M-75	0.86 (0.08) D	40	0.71 (0.04) D	20
PF-B-4	1.83 (0.21) B	100	1.54 (0.11) B	80
PF-B-13	1.82 (0.19) B	100	1.43 (0.12) B	80
PF-B-23	1.52 (0.14) C	90	0.91 (0.05) C	80
PF-B-38	1.08 (0.11) D	80	0.85 (0.07) C	70

[a] Standard deviations are presented in parentheses. The values in the same column with the same letter are not statistically different at $\alpha = 0.05$ according to the Duncan test. PF = phenol-formaldehyde.

than commercial phenol, and their amount is low (Effendi et al. 2008). As a result, the PF reaction may not be sufficient for the formation of a highly cross-linking resin network because of the shortage of phenol. Therefore, the wet strength of PF-M resins considerably decreased.

For PF-B resins, when the bio-oil addition percentage was 4 percent, the wet strength attained its highest value (1.54 MPa), although it was not significant compared with the wet strength of PF-B resin with 13 percent bio-oil substitution. In this case, the phenolic compounds in the bio-oil might serve as cross-linking agents due to the presence of multiple reactive sites (Hu et al. 2013). When the bio-oil addition percentage increased from 23 to 38 percent, the wet strength decreased. This should be attributed to the high viscosity of PF-B resins as shown in Table 4 and discussed above. Moreover, with the increasing amount of bio-oil, the relatively lower reactivity of bio-oil would dramatically retard resin curing as indicated by the gel time test results in Table 4.

Comparing crude bio-oil modified PF resin with blended PF resin, at lower bio-oil content levels of 10 and 25 percent, for the same amount of bio-oil (e.g., PF-M-10 resin and PF-B-4 resin), the wet bond strength of PF-M resin was significantly higher than that of PF-B resin. At a bio-oil content level of 50 percent, the wet bond strength of PF-M resin was the same as that of PF-B resin. However, at a higher bio-oil content level of 75 percent, for the same bio-oil amount (e.g., PF-M-75 resin and PF-B-38 resin), the wet bond strength of PF-B resin exceeded that of PF-M resin significantly. This trend was similar to that found in comparison to the dry bond strength of PF-M and PF-B resins. Further research is needed to explain these data.

Although for modified PF resin (PF-M resin), compared with the control PF resin, substituting phenol with 50 percent crude bio-oil resulted in the same dry bond strength and low wet strength, whereas with 25 percent bio-oil content, it resulted in both high dry and high wet bond strength. Therefore, this study showed that it was safe to substitute phenol with 25 percent crude bio-oil in modified PF resin without affecting both dry and wet bond strengths of a panel.

For the same reason, this study showed that it was safe to substitute PF resin with 13 percent crude bio-oil in blended PF resin without affecting both dry and wet bond strengths of plywood panels.

Conclusions

In this study, two types of PF resins were prepared and compared. For PF-M resins, crude bio-oil from pyrolysis of pinewood was synthesized with phenol and formaldehyde at 10, 25, 50, and 75 percent phenol substitution percentages, respectively. For PF-B resins, crude bio-oil was physically blended with PF resin at 4, 13, 23, and 38 percent addition percentages, respectively. The results indicated that incorporating crude bio-oil into PF resin either by synthesis or by blending at certain amounts could improve the bonding performance of PF resins. For PF-B resins, the best crude bio-oil addition percentage or PF resin substitute percentage was 13 percent, while for PF-M resins, the best phenol substitution percentage was 25 percent. Further increment in the crude bio-oil content level decreased the bond performance of both PF-M and PF-B resins. This was due mainly to increased viscosity and acidity of PF-B resins at a high crude bio-oil addition percentage and a shortage of reactive phenolic compounds in PF-M resins at a high phenol substitution percentage. Plywood bonded with the resins in this study could meet the requirement of Chinese Standard GB/T 17657-2013 and is suitable for outdoor applications, except for that bonded with PF-M-75 resin.

Based on the results of this study, it is suggested that the viscosity of PF resin blends be adjusted by adding solvents (or by other means) for higher wettability and penetration, that the final pH value be adjusted with alkaline for better curing results, that the PF resin synthesis method be optimized (such as choosing a new catalyst and modifying the reaction procedure), and that resin structure, curing behavior, and thermal stability be studied by instrumental analysis for fundamental support. Moreover, further study should focus on developing efficient and economic separation technology for the reactive phenolic compounds fraction in crude bio-oil, optimizing hot-pressing parameters for better panel performance, furthering the increment in the crude bio-oil content for a higher substitution and addition percentage, and expanding the application of crude bio-oil modified and blended PF resins to other wood engineering products.

Acknowledgments

Literature Cited

Aslan, M., G. Ozbay, and N. Ayrilmis. 2015. Adhesives characteristics and bonding performance of phenol formaldehyde modified with phenol-rich fraction of crude bio-oil. *J. Adhes. Sci. Technol*. 457(24):2679–2691.

Bu, Q., H. Lei, S. Ren, L. Wang, J. Holladay, Q. Zhang, J. Tang, and R. Ruan. 2011. Phenol and phenolics from lignocellulosic biomass by catalytic microwave pyrolysis. *Bioresour. Technol*. 102:7004–7007.

Bu, Q., H. Lei, L. Wang, Y. Wei, L. Zhu, Y. Liu, J. Liang, and J. Tang. 2013. Renewable phenols production by catalytic microwave pyrolysis of Douglas fir sawdust pellets with activated carbon catalysts. *Bioresour. Technol*. 142:546–552.

Celikbag, Y. and B. Via. 2015. Characterization of residue and bio-oil produced by liquefaction of Loblolly pine at different reaction time. *Forest Prod. J*. 66(1):29–36.

Chan, F., B. Riedl, X. Wang, X. Lu, C. Amen-Chen, and C. Roy. 2002. Performance of pyrolysis oil-based wood adhesives in OSB. *Forest Prod. J*. 52:31–38.

Chaouch, M., P. N. Diouf, A. Laghdir, and S. Yin. 2014. Bio-oil from whole-tree feedstock in resol-type phenolic resins. *J. Appl. Polym. Sci*. 131:596–602.

Choi, G., S. Oh, S. Lee, and J. Kim. 2015. Production of bio-based phenolic resin and activated carbon from bio-oil and biochar derived from fast pyrolysis of palm kernel shells. *Bioresour. Technol*. 178:99–107.

Dobele, G., T. Dizhbite, J. Ponomarenko, I. Urbanovich, J. Kreicberga, and V. Kampars. 2010. Isolation and characterization of the phenolic fractions of wood pyrolytic oil. *Holzforschung* 65:503–510.

Effendi, A., H. Gerharser, and A. V. Bridgwater. 2008. Production of renewable phenolic resins by thermochemical conversion of biomass: A review. *Renew. Sustain. Energy Rev*. 12(12):2092–2116.

Gardziella, A., A. Knop, and L. A. Pilato. 2000. Phenolic Resins: Chemistry, Application, Safety and Ecology. Springer-Verlag, Berlin.

Hu, X., Y. Wang, D. Mourant, R. Gunawan, C. Lievens, W. Chaiwat, M. Gholizadeh, L. Wu, X. Li, and C. Li. 2013. Polymerization on heating up of bio-oil: A model compound study. *Aiche J*. 59:888–900.

Jin Y., X. Cheng, and Z. Zheng. 2010. Preparation and characterization of phenol-formaldehyde adhesives modified with enzymatic hydrolysis lignin. *Bioresour. Technol*. 101:2046–2048.

Kim, J. S. 2015. Production, separation and applications of phenolic-rich bio-oil—A review. *Bioresour. Technol*. 178:90–98.

Li, Q., P. H. Steele, F. Yu, B. Mitchell, and E. B. M. Hassan. 2013. Pyrolytic spray increases levoglucosan production during fast pyrolysis. *J. Anal. Appl. Pyrolysis* 100:33–40.

Lu, Q., Z. Zhang, X. Yang, C. Dong, and X. Zhu. 2013. Catalytic fast pyrolysis of biomass impregnated with K_3PO_4 to produce phenolic compounds: Analytical Py-GC/MS study. *J. Anal. Appl. Pyrolysis* 104:139–145.

Mao, A., Z. He, H. Wan, and Q. Li. 2017. Preparation, properties, and bonding utilization of pyrolysis bio-oil. *In:* Bio-Based Wood Adhesives: Preparation, Characterization, and Testing. Z. He (Ed.). Science Publishers, CRC Press/Taylor & Francis Group, Boca Raton, Florida. pp. 260–279.

Mao, A., S. Q. Shi, and P. H. Steele. 2011. Flakeboard bonded with polymeric diphenylmethane diisocyanate/bio-oil adhesive systems. *Forest Prod. J*. 61:240–245.

Mohan, D., C. U. Pittman, and P. H. Steele. 2006. Pyrolysis of wood/biomass for bio-oil: A critical review. *Energy Fuels* 20:848–889.

Ozbay, G. and N. Ayrilmis. 2015. Bonding performance of wood bonded with adhesive mixtures composed of phenol-formaldehyde and bio-oil. *Ind. Crops Prod*. 66:68–72.

Pittman, C. U., D. Mohan, A. Eseyin, Q. Li, L. L. Ingram, Jr., E. M. Hassan, B. K. Mitchell, H. Guo, and P. H. Steele. 2012. Characterization of bio-oils produced from fast pyrolysis of corn stalks in an auger reactor. *Energy Fuels* 26:3816–3825.

Pocius, A. V. 2002. Adhesion and Adhesives Technology. Hanser, Cincinnati, Ohio.

Shahid, S. A., M. Ali, and Z. I. Zafar. 2014. Characterization of phenol-formaldehyde resins modified with crude bio-oil prepared from *Ziziphus mauritiana Endocarps*. *BioResources* 9:5362–5384.

Standardization Administration of the People's Republic of China (SAC). 2006. Test methods for wood adhesives and resins. GB/T 14074-2006. SAC, Beijing.

Standardization Administration of the People's Republic of China (SAC). 2013. Test methods of evaluating the properties of wood-based panels and surface decorated wood-based panels. GB/T 17657-2013. SAC, Beijing.

Sukhbaatar, B., P. H. Steele, and M. G. Kim. 2009. Use of lignin separated from bio-oil in oriented strand board binder phenol-formaldehyde resins. *BioResources* 4:789–804.

Yoshikawa, T., T. Yagi, S. Shinohara, T. Fukunaga, Y. Nakasaka, T. Tago, and T. Masuda. 2013. Production of phenols from lignin via depolymerization and catalytic cracking. *Fuel Process. Technol*. 108:69–75.

Zhang, Q., J. Chang, T. Wang, and Y. Xu. 2007. Review of biomass pyrolysis oil properties and upgrading research. *Energy Convers. Manag*. 48:87–92.