

# Improving Performance of Phenol-Formaldehyde Resins Modified/ Blended with Phenol-Rich Pyrolysis Bio-Oil

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## Abstract

In this study, we compare the panel performance of plywood made with phenol-formaldehyde (PF) resins modified and blended with phenol-rich bio-oil produced from pyrolysis of biomass. The modified PF resins were synthesized with phenol-rich bio-oil at phenol substitutions of 10, 25, 50, and 75 percent. The blended PF resins were prepared by blending control PF resin with phenol-rich bio-oil at 4, 13, 23, and 38 percent by weight. These resins were examined with Fourier-transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA) and evaluated as plywood binders. The results indicated that the apparent viscosities of modified PF resins were similar to those of control PF resin, while the apparent viscosities of blended PF resins increased with the addition of phenol-rich bio-oil. As the amount of phenol-rich bio-oil increased, the gel times of both modified and blended PF resins decreased first and then increased. FTIR results showed that modified PF resins with up to 25 percent substitution had FTIR spectra similar to those of control PF resin, while blended PF resins with a higher amount of added bio-oil had spectra more like those of bio-oil. TGA results showed that at temperatures of 25°C to 400°C, both modified and blended PF resins with high bio-oil content had better thermal stability than the control PF resin. Panel tests showed that modifying or synthesizing PF resin with phenol-rich bio-oil up to 50 percent increased both dry and wet bond strength. Blending PF resin with phenol-rich bio-oil up to 13 percent increased both dry and wet bond strength compared with control PF resin.

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Phenol-formaldehyde (PF) resins are important binders used in the wood panel industry with excellent heat and flame resistance, high tensile strength, and chemical resistance (Pizzi 2015, Wan et al. 2017). However, one of its raw materials, phenol, is normally a petroleum-derived chemical (Li et al. 2018). Finding alternative renewable resources for petroleum-derived chemicals can make their products more sustainable (Zhai et al. 2014, He et al. 2020, Wang et al. 2020, Yu et al. 2020). A promising potential source of chemical supply for PF resin is expected to be bio-oil (Li et al. 2020a). As a liquid product from pyrolysis of woody biomass, bio-oil has a typical water content of 15 to 30 percent and contains a large number of chemical compounds of various molecular weights, such as alcohols, aldehydes, ketones, sugars, organic acids, and phenols (20% to 25%; Mohan et al. 2006). The phenolic compounds in bio-oil are monomeric phenol and oligomeric polyphenols with various numbers of phenolic rings (Kim 2015).

The development of PF resin derived from bio-oil has been very active in the past decade. Two general approaches have been routinely used (Sukhbaatar et al. 2009, Mao et al. 2017). One is to replace phenol with bio-oil that has chemically synthesized phenolic resins; the other is to

physically blend PF resin with bio-oil to make resin mixtures. Our previous study (Mao et al. 2018) focused on the performance comparison of PF resins chemically modified with those physically blended with crude bio-oil, which was from pyrolysis of Chinese pinewood. The results indicated that incorporating certain amounts of crude bio-oil into PF resin by either synthesizing or blending improved the resin bonding performance compared with the control PF resin.

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Phenolic compounds in bio-oil are associated with the degradation of the lignin component and are expected to be important reactive components of PF reactions (Mohan et al. 2006). To obtain a higher concentration of reactive phenolic compounds, bio-oil is usually treated through several procedures, including hydrogenation, hydrodeoxygenation, catalytic cracking, steam reforming, molecular distillation, esterification, emulsification, or solvent extraction, prior to its application (Mao et al. 2011, 2017; Mao and Shi 2012). The treated bio-oil (phenol-rich bio-oil) is less acidic and contains fewer water-soluble compounds, and correspondingly, it is expected to replace commercial phenol at a higher percentage rate than crude bio-oil and result in better performance.

In this study, crude bio-oil from pyrolysis of pinewood (Chinese pine) was treated to obtain a phenol-rich bio-oil fraction by solvent extraction of PF resins modified and blended with phenol-rich bio-oil and compared with regard to aspects of physical property, chemical structure, thermal stability, and bonding strength. The results of this study were also compared with those obtained in our previous study (Mao et al. 2018). The objective of this study was to develop a sustainable bio-based PF resin with competitive performance for engineered wood panel manufacturing.

## Materials and Methods

### Materials

Phenol (99%), formaldehyde (37%), and sodium hydroxide (NaOH) were obtained from Sinopharm Group. Poplar (*Populus L.*) veneers with thicknesses of 1.6 to 1.7 mm and moisture content of 8 to 10 percent were obtained from a local plywood factory. Crude bio-oil was from a local bio-energy factory, where pinewood (Chinese pine) mixed with 10 percent bark was pyrolyzed in a fluidized-bed reactor.

### Phenol-rich bio-oil preparation

The bio-oil treatment procedure followed that described by Sukhbaatar et al. (2009). First, a certain amount of deionized water was added to crude bio-oil to separate a water-rich layer from a water-insoluble fraction of the bio-oil. Then the water-rich layer was removed. The remaining water-insoluble fraction was mixed with methanol in a 1:1 weight ratio to form a clear solution. A certain amount of deionized water was gradually added again to give a precipitate, which was viscous liquid with dark color. In this way, a phenol-rich fraction of bio-oil (phenol-rich bio-oil) was generated. The yield of phenol-rich bio-oil was approximately 28.5 percent based on crude bio-oil weight.

### Gas chromatography–mass spectrometry analysis of bio-oil

The chemical composition of bio-oil was analyzed by gas chromatography–mass spectrometry (GC-MS) with a Hewlett-Packard 5890/5971 GC-MS equipped with a ZB-5 capillary column (30 m by 0.32 mm inner diameter by 0.25- $\mu$ m film thickness). The GC oven temperature was initially held at 40°C for 5 minutes and then programmed to increase at 5°C/min to 280°C and then held for 20 minutes. The GC injector temperature was 280°C. The mass spectrometer utilized a 70-eV electron impact ionization mode with a source temperature of 260°C and an interface temperature of 270°C. Helium (99.99% purity) gas was utilized as the carrier gas at a flow rate of 1 mL/min.

### Resin preparation

Control PF resin with a formaldehyde to phenol (F/P) molar ratio of 2.0 was synthesized with phenol (P) charged once and formaldehyde charged twice (F<sub>1</sub> and F<sub>2</sub>). NaOH (40% solution) was divided into two portions (S<sub>1</sub> and S<sub>2</sub>) and charged with F<sub>1</sub> and F<sub>2</sub>, respectively. The weight ratio of F<sub>1</sub>:F<sub>2</sub>:S<sub>1</sub>:S<sub>2</sub> was 6:4:0.45:0.3. The calculated amounts of P, F<sub>1</sub>, and S<sub>1</sub> 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. Then the mixture was cooled to 70°C, and the calculated amounts of F<sub>2</sub> and S<sub>2</sub> were charged into the flask. The mixture was heated to 85°C and maintained until the viscosity of the mixture reached a range of 350 to 450 cP. The synthesized control PF resin was marked as PF-C (Table 1).

The modified PF resins were synthesized with phenol partially replaced with phenol-rich bio-oil at rates of 10, 25, 50, and 75 percent (based on the weight of phenol), respectively. The synthesis procedure was similar to that of PF-C resin. Phenol-rich bio-oil was charged together with 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 PF-C resin with phenol-rich bio-oil at rates of 4, 13, 23, and 38 percent (based on the weight of PF-C resin), respectively. 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 intentionally chosen to ensure the same amount of bio-oil contents in 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 amount of bio-oil. In this way, the comparison study between the two types of resins would be more meaningful and convincing.

### Resin properties evaluation

The apparent viscosities of the resins were measured at 25°C in accordance with Chinese National Standard GB/T 14074-2017 (Standardization Administration of China [SAC] 2017) using a DVS+ rotational viscometer (Brookfield Engineering Laboratories Inc.) The pH values of the

Table 1.—Resin preparation.<sup>a</sup>

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

<sup>a</sup> PF = phenol-formaldehyde.

resins were measured at 25°C in accordance with Chinese National Standard GB/T 14074-2017 (SAC 2017) with a PH5+ pH meter (EUtech Scientific Engineering GmbH). The gel times of the resins were measured at 100°C using boiling water in accordance with Chinese National Standard GB/T 14074-2017 (SAC 2017). The solid contents of the resins were measured by oven-drying the resin sample at 125°C for 2 hours. Three replicas were performed for each test.

### Fourier-transform infrared spectroscopy

The Fourier-transform infrared (FTIR) analysis of resins was measured with a TENSOR II spectrophotometer (Bruker Optik GmbH) to characterize PF-C, PF-M, and PF-B resins. During the process, the sample of a cured resin was located on the observation stage of the spectrophotometer. The FTIR spectra of a total of 64 scans for each sample from 4,000 to 600/cm wave number were recorded.

### Thermogravimetric analysis

The thermogravimetric analyses (TGA) of resins were performed with a Q50 instrument (TA Instruments) to characterize the thermal stabilities of cured PF-C, PF-M, and PF-B resins. For this test, all the resin samples were dried in a convective oven at 120°C for 3 hours. Specimens were placed in alumina crucibles and heated from 25°C to 600°C at a heating rate of 10°C/min. The flow rate of nitrogen purge gas was 20 mL/min. The TG curves of weight loss and derivative weight loss (DTG) were plotted.

### Panel manufacturing

Several pieces of three-layer poplar plywood samples with dimensions of 300 by 300 mm were manufactured using a laboratory hot press (XinXieLi Machine Manufacturing Co. Ltd). The resin application rate was 280 g/m<sup>2</sup> (double glue line), the same as in our previous study (Mao et al. 2018). The resins were applied uniformly on both sides of the middle veneer with a brush. The hot press time, temperature, and pressure were 5 minutes, 135°C, and 1.1 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 in accordance with 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 for the dry bonding strength test and the remaining six specimens for the wet bonding strength test. For the wet bonding strength test, specimens were first treated 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 cyclic treatment, the specimens were cooled down in water at 25°C and tested with a CMT 4104 universal testing machine (MTS System Corporation). The test results were averaged, and a standard deviation was provided. The wood failure percentages were measured and recorded.

### Statistical analysis

Means and standard deviations of the data obtained were calculated. One-way analysis of variance Duncan mean comparison tests with SPSS 22.0 software were used to determine the differences among resins.

## Results and Discussion

### Physical properties of phenol-rich bio-oil

The water content, pH, and apparent viscosity of phenol-rich bio-oil were 18.6 percent, 5.8, and 1,618 cP, respectively. Compared with the crude bio-oil used in our previous study (Mao et al. 2018), the phenol-rich bio-oil had lower water content (18.6% vs. 20.5%), higher pH value (5.8 vs. 2.6), and higher viscosity (1,618 vs. 1,468). Moreover, the concentrations of phenolic compounds in phenol-rich bio-oil were generally three to four times higher than those in crude bio-oil (see GC-MS results in Table 2).

### Chemical composition of phenol-rich bio-oil

Figure 1 shows the GC-MS chromatogram of phenol-rich bio-oil. A total of 22 volatile and semivolatile compounds were identified and quantified, similar to those in our previous study (Mao et al. 2018; Table 2), and 96 percent of the identified compounds were phenol, methylphenols, methoxyphenols, ethylphenols, propylphenols, and benzenediols. As expected, the concentrations of acids, aldehydes, alcohols, and ketones in this study were lower (4% vs. 73%), and the concentrations of phenolic compounds were higher (96% vs. 27%). The GC-MS results confirmed the phenol-rich feature of the treated bio-oil.

### Resin physical properties

Physical properties of PF-C, PF-M, and PF-B resins are presented in Table 3. For PF-M resins, the viscosities varied from 341 to 386 cP, similar to those of PF-C resin. This indicates that during the synthesis of PF-M resins, the viscosities were controlled well in the same way as for PF-C resin. However, the viscosities of PF-B resins increased with the addition of phenol-rich bio-oil from 457 cP at a 4 percent addition rate to 758 cP at a 38 percent addition rate due mainly to the highly viscous nature of phenol-rich bio-oil (1,618 cP).

The solid content of PF-M resins decreased with the increased amount of phenol-rich bio-oil (from 48.7% for PF-C resin to 44.5% for PF-M-75 resin). This could be attributed mainly to the relatively high water content of phenol-rich bio-oil (18.6%) compared with that of commercial phenol ( $\leq 1\%$ ). The solid contents of PF-B resins increased as expected with the amount of phenol-rich bio-oil (from 48.7% for PF-C resin to 57.9% for PF-B-75 resin) because phenol-rich bio-oil had much lower water content (18.6%) than the control PF-C resin (48.7%).

As the phenol substitution amount increased from 10 to 75 percent, the pH value of the PF-M resins varied slightly. The reason may be that the carboxylic acids in the phenol-rich bio-oil were partly neutralized by the alkaline added during the synthesis of PF-M resins. As the amount of phenol-rich bio-oil that was added increased from 4 to 38 percent, the pH of the PF-B resins decreased from 12.0 to 10.6 due to the relatively low pH value of the phenol-rich bio-oil (5.8) compared with that of PF-C resin (12.1).

Table 2.—Chemical composition of phenol-rich bio-oil.<sup>a</sup>

No.	Name of compound	Formula	Concentration in phenol rich bio-oil (wt%)	Data from Mao et al. (2018)	Category
1	Acetic acid	C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>	0.07 (↓)	5.65	Acid
2	Furfural	C <sub>5</sub> H <sub>4</sub> O <sub>2</sub>	0.02 (↓)	0.10	Aldehyde
3	2-methyl-2-cyclopenten-1-one	C <sub>6</sub> H <sub>8</sub> O	0.02 (↓)	0.08	Ketone
4	3-methyl-2-cyclopenten-1-one	C <sub>6</sub> H <sub>8</sub> O	0.01 (↓)	0.05	Ketone
5	Phenol	C <sub>6</sub> H <sub>6</sub> O	0.28 (↑)	0.11	Phenol
6	3-methyl-1,2-cyclopentanedione	C <sub>6</sub> H <sub>8</sub> O <sub>2</sub>	0.04 (↓)	0.34	Ketone
7	2-methylphenol	C <sub>7</sub> H <sub>8</sub> O	0.25 (↑)	0.05	Phenol
8	3-methylphenol	C <sub>7</sub> H <sub>8</sub> O	0.31 (↑)	0.07	Phenol
9	2-methoxyphenol	C <sub>7</sub> H <sub>8</sub> O <sub>2</sub>	1.21 (↑)	0.48	Phenol
10	2,4-dimethylphenol	C <sub>8</sub> H <sub>10</sub> O	0.29 (↑)	0.05	Phenol
11	3-ethylphenol	C <sub>8</sub> H <sub>10</sub> O	0.18 (↑)	0.04	Phenol
12	2,3-dimethylphenol	C <sub>8</sub> H <sub>10</sub> O	0.08 (↑)	0.03	Phenol
13	1,2-benzenediol	C <sub>6</sub> H <sub>6</sub> O <sub>2</sub>	1.31 (↑)	0.27	Phenol
14	5-(hydroxymethyl)-2-furaldehyde	C <sub>6</sub> H <sub>6</sub> O <sub>3</sub>	0.05 (↓)	0.37	Aldehyde
15	3-methyl-1,2-benzenediol	C <sub>7</sub> H <sub>8</sub> O <sub>2</sub>	0.36 (↑)	0.09	Phenol
16	4-ethyl-2-methoxy-phenol	C <sub>9</sub> H <sub>12</sub> O <sub>2</sub>	0.68 (↑)	0.27	Phenol
17	4-methyl-1,2-benzenediol	C <sub>7</sub> H <sub>8</sub> O <sub>2</sub>	0.72 (↑)	0.28	Phenol
18	Eugenol	C <sub>10</sub> H <sub>12</sub> O <sub>2</sub>	0.35 (↑)	0.15	Phenol
19	2-methoxy-4-propylphenol	C <sub>10</sub> H <sub>14</sub> O <sub>2</sub>	0.15 (↑)	0.07	Phenol
20	2-methoxy-4-(1-propenyl) phenol	C <sub>10</sub> H <sub>12</sub> O <sub>2</sub>	2.54 (↑)	0.83	Phenol
21	Oleic acid	C <sub>18</sub> H <sub>34</sub> O <sub>2</sub>	0.11 (↓)	0.74	Acid
22	Vanillin	C <sub>8</sub> H <sub>8</sub> O <sub>3</sub>	0 (↓)	0.35	Aldehyde

<sup>a</sup> Up and down arrows (↑ and ↓) in parentheses present the concentration variations of the compounds in phenol-rich bio-oil compared with those in crude bio-oil in Mao et al. (2018).

With the increase of phenol-rich bio-oil, the gel times of PF-M resins decreased first (from 379 s for PF-C resin to 348 s for PF-M-10 resin) and then increased quickly (from 348 s for PF-M-10 resin to 568 s for PF-M-75 resin). The decrease in gel time might be due to the increased F/P molar ratio when the phenol was substituted with the phenol-rich

bio-oil since there was less phenol in phenol-rich bio oil. However, as the substitution percentage exceeded 50 percent, PF-M resins had a gel time longer than that of PF-C resin, suggesting the low reactivity of phenol-rich bio-oil compared with phenol due to fewer free positions in the aromatic rings. For the PF-B resins, the trend was similar.

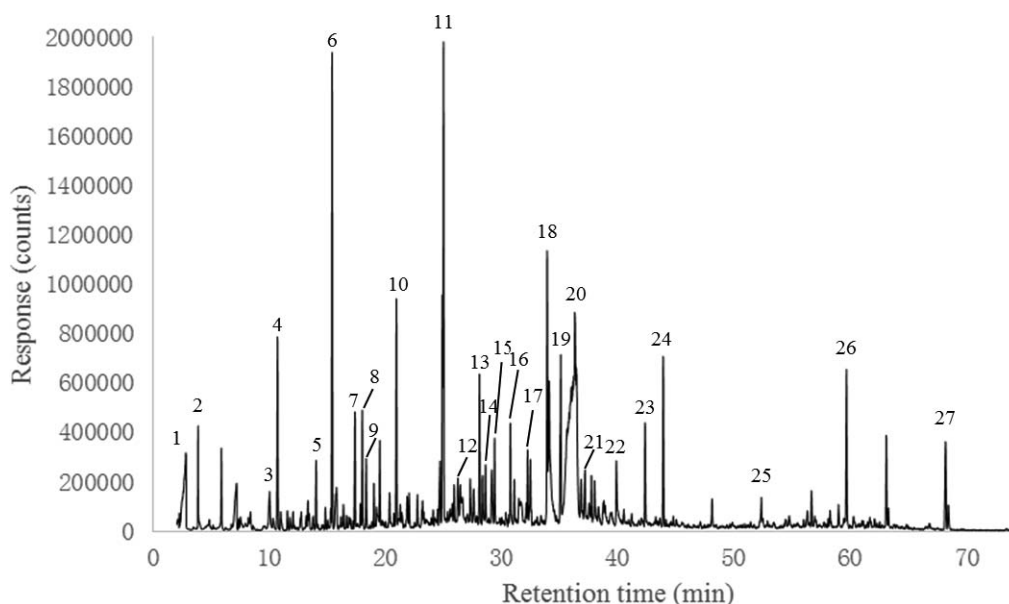


Figure 1.—Gas chromatography–mass spectrometry chromatogram of phenol-rich bio-oil: (1) acetic acid, (2) 1-hydroxy-2-propanone, (3) furfural, (4) methyl-2-cyclopentenone, (5) phenol, (6) 1,4-dichlorobenzene-d4 (internal standard), (7) 3-methyl-1,2-cyclopentanedione, (8) 2-methylphenol, (9) 3-methylphenol, (10) 2-methoxyphenol, (11) 2,4-dimethylphenol, (12) 3-ethylphenol, (13) 1,2-benzenediol, (14) 2,3-dimethylphenol, (15) 5-(hydroxymethyl)-2-furaldehyde, (16) 3-methyl-1,2-benzenediol, (17) 4-ethyl-2-methoxy-phenol, (18) 4-methyl-1,2-benzenediol, (19) acenaphthene-d10 (internal standard), (20) anhydrosugars, (21) 2-methoxy-4-propylphenol, (22) eugenol, (23) phenanthrene-d10 (internal standard), (24) 2-methoxy-4-(1-propenyl) phenol, (25) oleic acid, (26) chrysene-d12 (internal standard), (27) perylene-d12 (internal standard).

Table 3.—Physical properties of the resins.<sup>a</sup>

Resin code	Viscosity (cP)	pH	Solid content (wt%)	Gel time (s)
PF-C	378 (378)	12.3 (12.3)	48.7 (48.7)	379 (379)
PF-M-10	352 (332)	11.8 (11.4)	47.9 (47.5)	348 (355)
PF-M-25	341 (334)	11.5 (10.2)	47.2 (46.5)	370 (376)
PF-M-50	346 (327)	11.6 (10.3)	46.1 (45.3)	398 (441)
PF-M-75	386 (367)	11.4 (10.7)	44.5 (43.7)	568 (638)
PF-B-4	457 (418)	12.0 (11.7)	49.8 (48.6)	365 (370)
PF-B-13	516 (465)	11.7 (11.3)	52.6 (50.6)	320 (333)
PF-B-23	602 (512)	11.2 (10.7)	54.7 (53.8)	385 (406)
PF-B-38	758 (599)	10.6 (9.5)	57.9 (56.7)	451 (482)

<sup>a</sup> Data in parentheses were adapted from Mao et al. (2018). PF = phenol-formaldehyde.

The decrease in gel time might be attributed to the presence of high-molecular-weight phenolic compounds in phenol-rich bio-oil, as it is a general rule that thermosetting resins with higher molecular weight cure faster because of the lower activation energy needed (Aslan et al. 2015). As indicated in the GC-MS results (Table 2), phenol-rich bio-oil contained phenol and its derivatives. Most of these phenolic compounds had higher molecular weight than phenol and might promote cross-linking and result in resin gelling (Hu et al. 2013). As the addition of phenol-rich bio-oil exceeded 13 percent, the increase in gel time might be attributed to the low polymerization reactivity of the PF-B resins, and pH values decreased as well.

Compared with the results of our previous study (Mao et al. 2018; Table 3), the modified/blended PF resins prepared in this study generally had higher viscosities, pH values, and solid contents but shorter gel times. This could be due to higher viscosity, higher pH value, and higher phenol concentration as well as the lower water content of phenol-rich bio-oil compared with those of crude bio-oil in our previous study (Mao et al. 2018).

### FTIR spectra of the resins

The FTIR analysis of PF-C and PF-M resins is shown in Figure 2. The broad characteristic band detected at around 3,346.9/cm was attributed to aromatic and aliphatic -OH groups (Aslan et al. 2015). The FTIR spectra of PF-C, PF-M-10, and PF-M-25 resins were similar. Most of the bands appearing in the spectrum of PF-C resin were also observed in the spectra of PF-M-10 and PF-M-25 resins with only minor differences in intensity, indicating that substituting phenol with phenol-rich bio-oil at percentages up to 25 percent did not obviously change the structure of PF-C resin. This observation is in agreement with a previous study (Wang et al. 2009). However, as the substitution percentage continuously increased, the spectra of PF-M-50 and PF-M-75 resins became complicated and showed new bands at around 2,937.1 and 1,697.5/cm, respectively. This was attributed to the presence of alkane groups in the phenol-rich bio-oil, showing that the aliphatic structures in the bio-oil components of PF-M resins were more dominant (Majid and Pihillagawa 2014).

The FTIR analysis of PF-C and PF-B resins is shown in Figure 3. The spectra of PF-B-4, PF-B-13, PF-B-23, and PF-B-38 resins showed larger differences from those of PF-C resin with more bands of various intensity detected in the

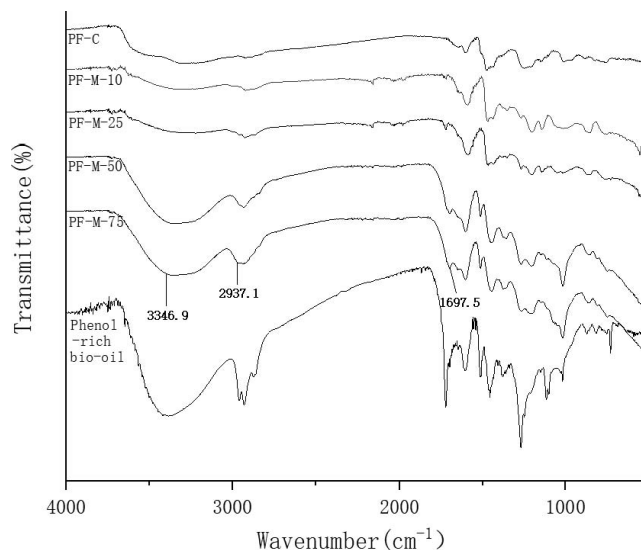


Figure 2.—Fourier-transform infrared spectroscopy spectra of PF-C and PF-M resins.

spectra. With the increase in the amount of phenol-rich bio-oil, the intensity of bands at 3,385.4/cm obviously increased, indicating the increased aromatic and aliphatic -OH group concentrations and thus showing the increased amount of the unreacted phenol components of PF-B resins. Compared with the spectra of PF-M resins, the spectra of PF-B resins had more characteristics similar to those of bio-oil instead of PF-C resin (Patel et al. 2011).

### TGA of the resins

The thermal stability of cured PF-C, PF-M, and PF-B resins was evaluated by TGA. The TG and DTG curves of PF-C and PF-M resins are shown in Figure 4. Based on the results, PF-C resin had three different weight loss ranges as indicated by the DTG curve, showing that PF resin

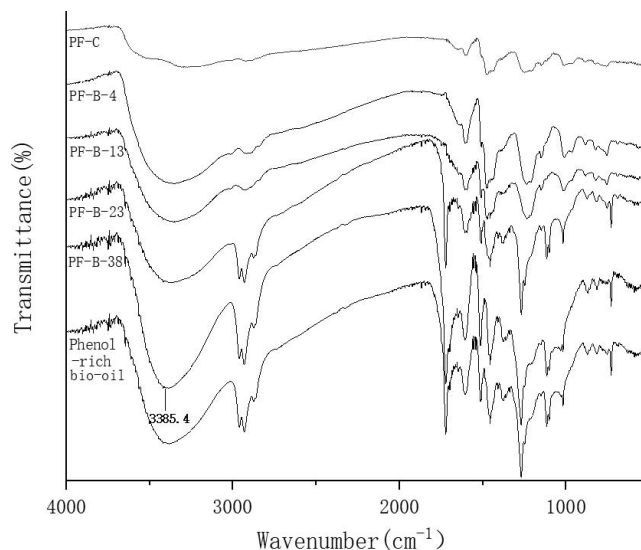


Figure 3.—Fourier-transform infrared spectroscopy spectra of PF-C and PF-B resins.

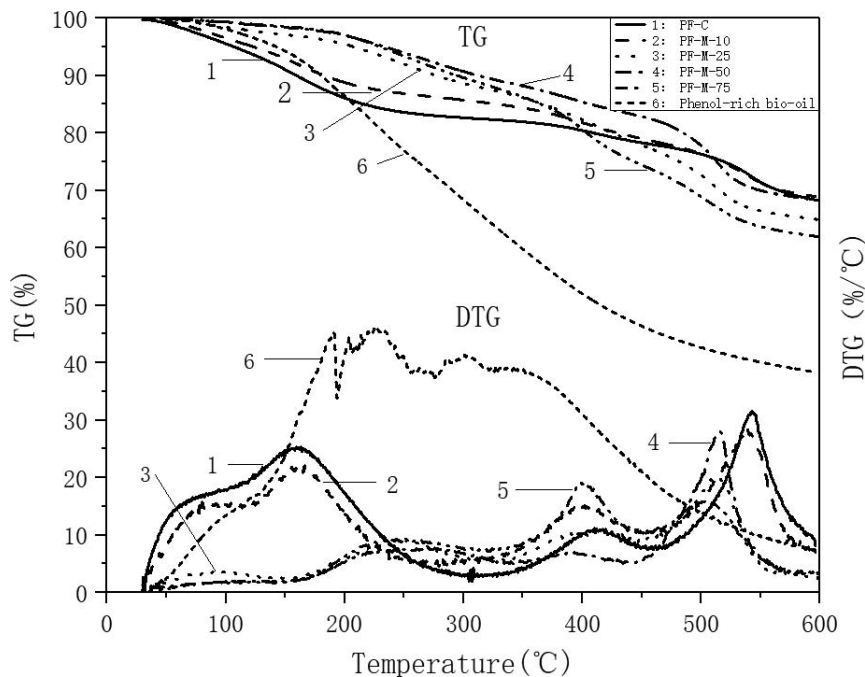


Figure 4.—Thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of PF-C and PF-M resins.

experienced three major thermal events: postcuring, thermal reforming, and ring stripping. The first range occurred between 30°C and 300°C with a relatively high weight loss rate. The weight loss might include the evaporation of free formaldehyde, free phenol, and those formed from the postcuring of PF resins. The second range started from 300°C to 450°C, where the weight loss rate became much lower, indicating that a slow degradation process occurred. The weight loss might be due to the degradation of the methylol groups and the methylene bridges. The third range started from 450°C to 600°C, where the weight loss rate increased, indicating that a fast weight loss process occurred. The weight loss might be due to the releases of carbon monoxide and methane that were formed through reactions between water, hydrogen, and the methylene groups. The three weight loss ranges of PF-C resin were similar to the results of other studies (Lee et al. 2012, Chaouch et al. 2014).

PF-M-10 resin had a similar weight loss behavior to that of PF-C resin. However, within the temperature range of 25°C to 500°C, PF-M-10 resin had lower weight loss than that of PF-C resin, indicating a better thermal stability of PF-M-10 at this temperature range. The curves of PF-M-25, PF-M-50, and PF-M-75 resins were quite different from those of PF-C and PF-M-10 resins at four temperature ranges in DTG curves. Within the temperature range of 25°C to 400°C, PF-M-25 and PF-M-75 resins had better thermal stabilities than that of PF-C resin. At the temperature range of 25°C to 500°C, PF-M-50 resin had the best thermal stability among PF-C and PF-M resins. At higher temperature, PF resins, especially PF-M-25, PF-M-50, and PF-M-75 resins, had high weight loss rates. This might be attributed to the weak cross-linked networks of PF resins and the breakdown of aliphatic side chains presented in the molecules of bio-oil as indicated by the FTIR analysis (Fig. 2; Chaouch et al. 2014).

The TG and DTG curves of PF-C and PF-B resins are shown in Figure 5. The PF-B-4 and PF-B-13 resins seemed to have weight loss curves similar to those of PF-C resin, while PF-B-23 and PF-B-38 resins had different weight loss. At a lower temperature range (from 25°C to around 350°C), thermal stability of PF-C, PF-B-4, and PF-B-13 was lower than that of PF-B-23 and PF-B-38 resins. This might be attributed to the relatively high amount of pyrolytic lignin fraction in phenol-rich bio-oil, which started to decompose at a temperature of around 350°C (Mohan et al. 2006). However, at temperatures higher than 400°C, PF-B-23 and PF-B-38 resins showed higher weight losses than the other three resins. This might also be due to the degradation of the large amount of pyrolytic lignin fraction in phenol-rich bio-oil (Mohan et al. 2006).

Combining Figures 2 and 3, TGA showed that at the lower temperature range (up to 400°C), PF resins with higher phenol-rich bio-oil percentages showed better thermal stability, while at the higher temperature range (from 500°C to 600°C), PF resins with lower phenol-rich bio-oil percentages showed less weight loss.

### Panel bonding performance

The bond strength and wood failure of the resins are presented in Table 4. Compared with PF-C resin, synthesized PF resins (M-10/M-25/M-50) increased both dry and wet bond strength of the plywood panels. The wood failure performance was same. PF-M resins were clear, dark brown, liquid resins with good homogeneity and good fluidity and correspondingly could spread well on the veneer surface. This could be one reason for their resulting in good dry bond strength (Jin et al. 2010; Li et al. 2017, 2020b). Moreover, partial substitution of phenol with phenol-rich bio-oil would increase the F/P molar ratio, resulting in a higher cross-linking network with possible better water resistance. This might also be a factor contributing to wet bond strength.

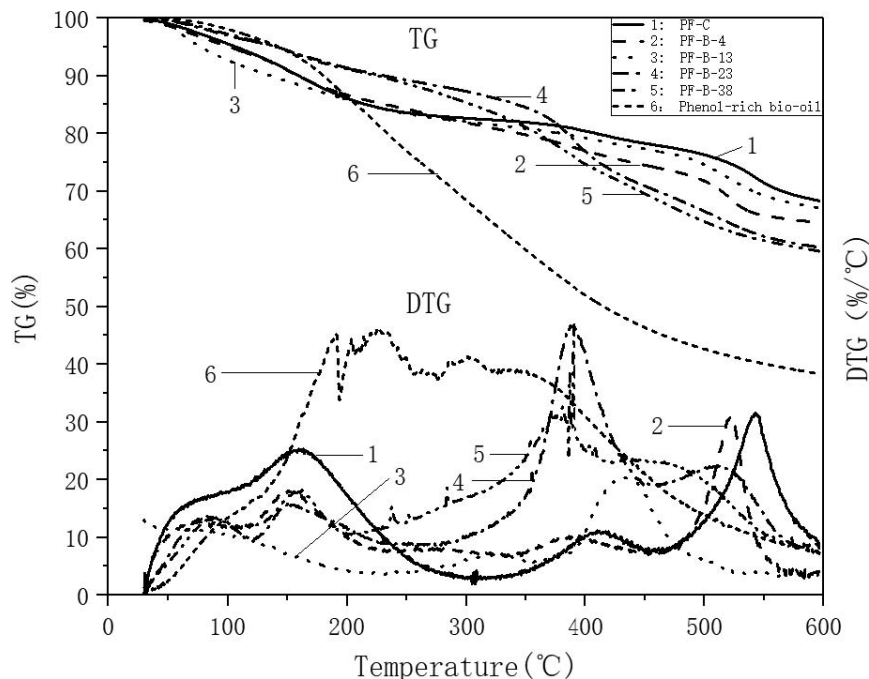


Figure 5.—Thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of PF-C and PF-B resins.

However, at a substitution percentage of 75 percent, both the dry and the wet bond strength of PF-M resin decreased, as did the wood failure. This might be attributed to a less cross-linked PF resin structure because of the shortage of reactive sites in polyphenols compared with commercial phenol (Effendi et al. 2008).

Blending PF resin with phenol-rich bio-oil up to 13 percent increased both dry and wet bond strength (Table 4). Phenolic compounds in the bio-oil might serve as cross-linking agents due to the presence of multiple reactive sites to promote resin curing (Hu et al. 2013). This might contribute to better dry and wet bond strength. However, statistical analysis showed that at higher percentages (23% and 38%), the dry and wet bond strength of PF-B resins decreased significantly. This might be attributed to the increased viscosity of PF-B resins (Table 3), which would affect the wettability of resin to the veneer surface, the

flowability of resin on the wood surface, and the penetration of resin into the wood as indicated by the wood failure at higher substitution rates. Moreover, with the increase of phenol-rich bio-oil, the relatively lower reactivity of bio-oil would obstruct resin curing (Table 3).

In comparison with the bond performance results in our previous study (Mao et al. 2018; Table 4), the PF-M resins prepared in this study generally showed higher dry and wet bond strength, confirming our hypothesis. Especially at a percentage of 50 percent, PF resin modified by phenol-rich bio-oil showed much higher dry and wet bond strength values than that modified by crude bio-oil in our previous study (Mao et al. 2018). The PF-B resins prepared in this study showed dry and wet bond strength comparable to that in our previous study only at a percentage up to 13 percent. This comparison of bond strength shows that phenol-rich bio-oil in the synthesis of PF resin could be adding up to 50

Table 4.—Bonding performance of the panels.<sup>a</sup>

Resin code	Dry strength (MPa)	Wood failure (%)	Wet strength (MPa)	Wood failure (%)	Data from Mao et al. (2018)	
					Dry strength (MPa)	Wet strength (MPa)
PF-C	1.52 (0.13) C (C)	100	1.47 (0.14) C (c)	90	1.52 (C)	1.47 (c)
PF-M-10	1.89 (0.12) B (B)	100	1.72 (0.07) B (b)	100	1.84 (B)	1.67 (b)
PF-M-25	2.14 (0.18) A (A)	100	1.88 (0.12) A (a)	100	2.09 (A)	1.75 (b)
PF-M-50	2.12 (0.11) A (A)	100	1.71 (0.06) B (b)	100	1.58 (C)	0.87 (d)
PF-M-75	1.29 (0.09) D (D)	50	0.87 (0.06) D (d)	50	0.86 (E)	0.71 (d)
PF-B-4	1.84 (0.17) B (B)	100	1.59 (0.13) C (c)	100	1.83 (B)	1.54 (c)
PF-B-13	1.79 (0.15) B (B)	100	1.52 (0.13) C (c)	80	1.82 (B)	1.43 (c)
PF-B-23	1.35 (0.12) D (D)	80	0.95 (0.06) D (d)	80	1.52 (C)	0.91 (d)
PF-B-38	0.93 (0.15) E (E)	80	0.78 (0.09) D (d)	50	1.08 (E)	0.85 (d)

<sup>a</sup> Values in parentheses are standard deviations. Data in the same column with the same character are not different at  $\alpha = 0.05$ . Data in the second and sixth columns with the same character in parentheses are not different at  $\alpha = 0.05$ . Data in the fourth and seventh columns with the same character in parentheses are not different at  $\alpha = 0.05$ . PF = phenol-formaldehyde.

percent with considerable improvements in bond performance. It also showed that although blending PF with phenol-rich bio-oil at a percentage up to 13 percent could result in better bond performance than the control PF resin, this is not necessary since it did not perform better than the crude bio-oil.

## Conclusions

In this study, two types of PF resins were prepared and compared. The PF-M resins were synthesized with phenol-rich bio-oil at phenol substitution percentages of 10, 25, 50, and 75 percent. The PF-B resins were prepared by blending PF resin with phenol-rich bio-oil at percentages of 4, 13, 23, and 38 percent. The obtained resins were examined with FTIR and TGA and evaluated as plywood binders. The following results were obtained: (1) The viscosities of PF-M resins were similar to that of control PF resin, while the viscosities of PF-B resins increased with the amount of phenol-rich bio-oil due to its high viscosity. With an increase of phenol-rich bio-oil, the gel times of both PF-M and PF-B resins first decreased and then increased. (2) The FTIR results indicated that substituting phenol with phenol-rich bio-oil at a percentage up to 25 percent did not obviously change the structure of PF resin. At higher bio-oil addition percentages, the spectra of PF-B resins had more bio-oil characteristics. (3) The TGA showed that at a lower temperature range (up to 400°C), PF resins with higher phenol-rich bio-oil percentages showed better thermal stability, while at a higher temperature range (from 500°C to 600°C), PF resins with lower phenol-rich bio-oil percentages showed less weight loss. (4) Panel test results showed that synthesizing PF resin with phenol-rich bio-oil at a percentage up to 50 percent increased both dry and wet bond strength. Blending PF resin with phenol-rich bio-oil at a percentage up to 13 percent increased both dry and wet bond strength of PF-C resin. Further increments in the bio-oil content level decreased the bond performance of both PF-M and PF-B resins.

Compared with PF resin made with crude bio-oil, using phenol-rich bio-oil in the preparation of PF resins resulted in resins with comparable or even better performance. For modified PF resins, the substitution percentage of phenol-rich bio-oil could be increased to up to 50 percent with better bond performance. For blended PF resins, the addition percentage of phenol-rich bio-oil could be up to 13 percent with bond performance comparable with that in our previous study.

Further study will be focused on the development of an alternative PF resin synthesis method for better resin properties, the optimization of hot pressing parameters for better panel performance, and the expansion of the application of bio-oil modified/blended PF resins to other engineered wood products.

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