Use of Biocrude Derived from Woody Biomass to Substitute Phenol at a High-Substitution Level for the Production of Biobased Phenolic Resol Resins

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ABSTRACT: Phenolic bio-oil produced by the direct liquefaction of Eastern white pine (*Pinus Strobus L.*) sawdust in a hot-compressed ethanol-water (1:1 w/w) medium at 300 °C was used to partially substitute for phenol in the synthesis of bio-oil-phenol-formaldehyde (BPF) resol resins. Bio-based resol resins with high levels of phenol substitution (up to 75 wt%) could be used as plywood adhesives because of the low molecular weights found for the phenolic bio-oil (weight-average molecular weight = 1072 g/mol, number-average molecular weight = 342 g/mol). The properties of the BPF resol resins were analyzed by differential scanning calorimetry, Fourier transform infrared spectroscopy, gel permeation chromatography, and thermogravimetric analysis. All of the experimental BPF resins possessed broad molecular weight distributions but had similar chemical/thermal properties compared to a conventional phenol–formaldehyde (PF) resol resin reference (or 0 wt % BPF resin). The BPFs exhibited the typical properties of a thermosetting PF resin, for example, an exothermic curing temperature of 140–150°C and an acceptable residual carbon yield of 48–72 wt % nonvolatile content at 700°C. The experimental BPFs were applied as adhesives in the assembly of plywood, and then, the dry/wet tensile strengths were evaluated. The tensile strengths of the dry plywood samples bonded with the BPF resins up to a high ratio value of 75 wt % bio-oil exceeded or were comparable to that of the conventional pure PF resin adhesive. All of the BPF-resin-bonded plywood samples gave wet tensile strengths comparable to those of the conventional PF adhesive. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 2743–2751, 2011

Key words: adhesives; biopolymers; curing of polymers; resins; thermal properties

INTRODUCTION

Phenol–formaldehyde (PF) resins are most widely used as wood adhesives in the manufacturing of engineered wood products, such as plywood, laminated veneer lumber, particle boards, Oriented Strand Board (OSB), and fiberboards. PF resins are also used in different industrial products, such as insulation, coated abrasives, paper saturation, and floral foam. In today's society, where petroleum prices are high, petroleum resources are depleted; this is coupled with an increased demand for petroleum from developing economies and provides a dire situation. There are also political and environmental concerns over fossil-based resources; this has intensified interest in the research and development of alternative, renewable (nonpetroleum) resources to substitute for phenol in the manufacturing of PF-type adhesives.

Forest/agricultural biomass or residues are lignocellulosic materials containing about 10–35 wt % lignin, 35–45 wt % cellulose, and 15–35 wt % hemicellulose.[1–4] Lignin is the second most abundant polymer found in nature and is a major waste product of the paper industry (50 million tons is produced per year). Lignin is an amorphous macromolecule comprised of three phenyl propanols, that is, *p*-hydroxyl phenyl propanol, guaiacyl propanol, and syringyl propanol, which are linked together by condensed linkages (e.g., 5-5 and β-1 linkages) and ether linkages (e.g., β-*O*-4 and α-*O*-4 linkages). This macromolecule can be decomposed/degraded into oligomeric and monomeric phenolic compounds through thermochemical technologies, such as hydrolysis, pyrolysis, and direct liquefaction.[5–9] In this regard, lignocellulosic biomass can be a potential source of biophenols to replace

petroleum-based phenols in the production of PF resins. In the past decade, researchers have given considerable effort to partially replacing petroleum-based phenols with lignins, tannins, and liquefied biomass, such as pyrolysis oil and biocrude from direct liquefaction processes.[10–12] Pyrolysis oils are a complex mixture of water (15–35 wt %) and organics with high oxygen contents (45–50 wt %). This oxygen content is distributed throughout hundreds of compounds, such as hydroxyaldehydes, hydroxyketones, sugars, carboxylic acids, and phenolics.[8] Pyrolysis oils are, thus, unstable for storage. Additionally, the phenolic compounds in pyrolysis oils are mainly fragments of lignin from large-molecular-weight molecules. This makes them less reactive in PF resin synthesis reactions because of the shortage of reactive sites and the steric hindrance of large molecules. In the synthesis of a PF resin with an alkaline catalyst, phenols are deprotonated to form phenoxide ions, and the electron-rich ortho and para positions in the phenoxide ions are more susceptible to electrophilic aromatic substitution by the hydrated form of formaldehyde (often referred to as an *addition reaction*). Therefore, pyrolysis oils were found to be less effective in the substitution of phenol for PF resin synthesis. In the production of practically useful biobased PF resins, the ratios are normally below 30–50 wt % phenol.[10–12]

The direct liquefaction of biomass or solvolytic liquefaction technologies have attracted increasing interest for the production of biophenol precursors to substitute for phenol in the synthesis of biobased phenolic resins.[13–15] Direct liquefaction processes are generally more advantageous than pyrolysis processes with respect to the energy efficiency and quality (e.g., molecular weights) of the liquid products. However, bio-oils from many low-temperature solvolytic processes with phenol or ethylene glycol catalyzed by H_2SO_4 are still of much lower reactivity than pure phenol in the synthesis of phenolic resins. This is because of their shortage of monophenolic compounds with unoccupied ortho and para positions[16] and because the liquid products from the low-temperature solvolytic processes are rich in large molecules of oligomers derived from lignin and cellulosic components. In a recent research,[17] we investigated a high-temperature direct liquefaction process using cosolvents of water and ethanol. White pine sawdust was effectively liquefied in a 50 wt % ethanol–water medium; this produced approximately 66 wt % bio-oil and a biomass conversion greater than 95% at 300°C for 15 min.[17] The obtained bio-oil had a weight-average molecular weight (M_w) of 1373 g/mol and a number-average molecular weight (M_n) of 630 g/mol; these values were much lower than those of pyrolysis oils. As such, the bio-oil could be a promising biophenol precursor to substitute for phenol at a higher substitution level for the production of bio-oil PF resins and adhesives.

In this study, phenolic bio-oil produced by the direct liquefaction of Eastern white pine (*Pinus strobus L.*) sawdust in a hot-compressed ethanol–water (1 : 1 wt/wt) medium at 300°C was used to partially substitute for phenol to a high level (up to 75 wt %) for the synthesis of bio-oil–phenol–formaldehyde (BPF) resol resins. The experimental BPFs were characterized by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), gel permeation chromatography (GPC), and Fourier transform infrared spectroscopy. The obtained BPFs were applied as adhesives to the assembly of plywood. The dry/wet tensile strengths of the plywood samples bonded with the BPF resins were compared and evaluated against conventional pure PF resins.

EXPERIMENTAL

Materials

The woody biomass used in this study was Eastern white pine sawdust obtained from a local sawmill in Thunder Bay, Ontario, Canada. The woody biomass sample was subject to compositional analysis for its contents of cellulose, hemicelluloses, and lignin. The tests were done in accordance with TAPPI T249cm-85 test method (for cellulose and hemicellulose) and TAPPI T222 om-88 test method (for acid-soluble and acid-insoluble lignin). From the analysis, we found that the white pine sawdust contained 28.4 wt % lignin, 40.2 wt % cellulose, and 21.9 wt % hemicellulose. The sawdust sample was oven dried at 105°C for a period of 24 h before use. The solvents and chemicals used in this study were distilled water, American Chemical Society reagent-grade ethanol (Fisher Scientific, Batesville, IN), acetone (Fisher Scientific, Fair Lawn, NJ), solid phenol crystal (99%, J. T. Baker, Phillipsburg, NJ), a sodium hydroxide solution (ca 50%, Ricca Chemical Co., Arlington, TX), and formaldehyde (ca 37%, Anachemia, Montreal, QC). In the GPC analysis for the liquid products, High Performance Liquid Chromatography (HPLC) grade solvent tetrahydrofuran (THF, Malinckrodt Baker, Phillipsburg, NJ) containing 0.03% stabilizer of 2,6-di-*t*-butyl-4-methyl phenol and American Chemical Society reagent-grade pyridine and acetic acid (Sigma-Aldrich, St. Louis, MO).

Preparation of phenolic bio-oil from woody biomass by direct liquefaction

The details of the liquefaction process were given in a previous article.[17] In brief, the liquefaction of pine sawdust was carried out in a 1000-mL stainless steel autoclave reactor equipped with a stirrer and a water-cooling coil. In a typical run, the reactor was charged with 50 g of pine sawdust and 500 g of ethanol–water

(1 : 1 w/w) cosolvent. The reactor was sealed, and the air inside the reactor was displaced by high-purity nitrogen. The reactor was subsequently pressurized to 2.0 MPa with nitrogen to prevent the reactive material from boiling during the course of heating. The reactor was heated to the desired temperature at a steady rate of 10°C/min and soaked at the reaction temperature for 15 min before it was cooled. Once the reactor was cooled to room temperature with the water-cooling coil, the gaseous products inside the reactor were vented. The liquid products and solid residue in the reactor were filtered and separated with acetone. The ethanol and acetone in the filtrate solution were then removed by rotary evaporation *in vacuo* at 40°C, whereas the remaining liquid solution was extracted with ethyl acetate with a separatory funnel. Under a reduced pressure at 57°C, ethyl acetate was removed to recover the liquid oily products, denoted as *bio-oil.* The bio-oil was used as the biophenol precursors to substitute for phenol for the synthesis of BPF resol resins. The obtained bio-oil had an M_w of 1072 g/mol and an M_n of 342 g/mol, as determined by GPC analysis.

Synthesis of the BPF resol resins with woody-biomass-derived bio-oil

Various BPF resol resins with different bio-oil ratios (25, 50, and 75 wt %) were synthesized in a 100-mL, three-necked flask equipped with a pressure-equalizing addition funnel, thermometer, cooling condenser, and water bath with a magnetic stirrer. These biobased resol resins were denoted as 25% BPF, 50% BPF, and 75% BPF. A control reference sample with pure phenol (0 wt % bio-oil) and denoted as PF resin was also prepared. In a typical run, 10 g of bio-oil/phenol, 4 g of water, 2 g of a 50 wt % sodium hydroxide solution (10 wt % phenolic feed), and 10 mL of ethanol were charged into the flask. The mixture was heated to 80°C and maintained at this temperature for 2 h under stirring to maintain a homogeneous solution. After this, 11.2 g of formaldehyde (ca 37 wt %) was added dropwise to the flask through a pressure-equalizing addition funnel. If the bio-oil was identified as containing phenols, the added formaldehyde was added correspondingly with a molar ratio of formaldehyde to phenols of 1.3. After condensation for 2 h, the reaction was stopped by rapid cooling in a water bath until room temperature was reached.

Characterization of the BPF and PF resol resins

The viscosity of all of the phenolic resins was measured at 50°C by Brookfield CAP 2000+ viscometer (Brookfield Engineering Laboratories, Middleboro, MA) according to ASTM D 1084-97. The nonvolatile contents of the resol resins were determined at 125°C for 105 min according to ASTM D 4426-01. The free formaldehyde levels in the resins were determined with a modified Walker's hydroxylamine hydrochloride method.[18] Approximately 2 g of resin was diluted with 25 mL of water, and the pH was adjusted to 4.0 with 0.1M HCl. Thirty milliliters of hydroxylamine hydrochloride (0.5M, pH = 4.0) was added to the resin solution, and the mixture was stirred for 10 min. Free formaldehyde was determined by back titration to pH 4.0 with 0.1M aqueous sodium hydroxide. The remaining free phenol in the resins was measured by HPLC (1525 binary HPLC pump, Bio-Rad HPX-87H column at 65°C) with a 0.01M H_2SO_4 water solution as the eluent at a flow rate of 0.8 mL/min. The thermal curing properties of the resins were evaluated with a Differential scanning calorimeter (DSC 1, Mettler-Toledo, Schwerzenbach, Switzerland) under 50–60 mL/min of N_2 at four different heating rates (5, 10, 15, and 20°C/min) between 40 and 250°C in a sealed aluminum crucible. The thermal stability of the resins was determined on a TGA instrument (TGA 1000i, Instrument Specialists, Inc. Twin lakes, WI) from 25 to 700°C. The nonvolatile resin sample ($\sim$ 10 mg) was heated in a platinum pan at a heating rate of 10°C/min under 30 mL/min of N_2.

The IR spectroscopy of the resins was recorded on an IR2000 spectrometer (PerkinElmer, Waltham, MA) Waters Breeze gel permeation chromatograph (Waters, Milford, MA, 1525 binary HPLC pump, UV detector at 270 nm, Waters Styrange HR1 column at 40°C) with THF as the eluent at a flow rate of 1 mL/min, and polystyrene was used as the calibration standard. To improve the resin's solubility in THF solvent, all of the resin samples were subjected to acetylation by the dissolution of 0.5 g of resin in 10 mL of a mixture (1 : 1 v/v) of pyridine and acetic acid followed by magnetic stirring at room temperature for 24 h. Acetylated products were obtained by precipitation in ice-cooled 1.0 wt % HCl solution and then filtered, rinsed thoroughly with distilled water, and vacuum-dried at room temperature.

Evaluation of the tensile strength of the plywood samples bonded with BPF resins

All of the synthesized phenolic resol resins were further tested as adhesives for manufacturing of three-layer plywood. Yellow birch veneers (11 × 11 × 1/16 in.[3]) were conditioned at 20°C and 60% relative humidity to reach a 10–12% moisture content (MC). The resin mixed with wheat flour (15 wt % resin)was applied with a brush to the inside surface of the two face veneers at a spread rate of 250 g/m^2

TABLE I
Physical Properties of the BPF and PF Resol Resins

Type of resol resins	pH values	Nonvolatile contents (wt %)[a]	Free phenol (wt %)	Viscosity (cp)[a]	Free formaldehyde (wt %)[b]
Pure PF	10.5	35.4 (± 1.2)	6.2	18.4 (± 0.03)	ND[c]
25% BPF	9.6	37.7 (± 0.2)	—	19.5 (± 0.01)	0.19 (± 0.003)
50% BPF	10.0	38.3 (± 0.3)	< 0.1	21.0 (± 0.01)	0.51 (± 0.01)
75% BPF	9.5	38.1 (± 0.2)	—	29.5 (± 0.01)	0.67 (± 0.01)

[a] Each value represents an average of three samples.
[b] Each value represents an average of two samples.
[c] ND, not detected.

per single glue line. After this, the two-faced surface veneers were kept at room temperature for about 1 h to remove any MC in the adhesives before hot pressing. The face and center veneer were bonded in directions perpendicular to each other with a hot press at 140°C under 2500 psi for 4 min. To obtain a better statistical significance with regard to the measurements, two panels were manufactured for each sample. In accordance with ASTM D 906-98, 20 specimens were cut from each panel for tensile strength testing in such a way as to ensure that for half the specimens, lathe checks were pulled in the open direction; for the other half, lathe checks were pulled in the closed direction. Half of the specimens of each sample, including 10 in the open direction and 10 in the closed direction, were tested after conditioning (to get 10–12% MC). In addition, 20 specimens were boiled for 3 h before testing to investigate the wet tensile strength and water resistance for all of the resins. The specimens were tested for shear stress by tension loading until failure with a Bench-top universal testing machine (Model H10K-T UTM, Tinus Olsen Material Testing Machine Co. Horsham, PA) at a loading rate of 10 mm/min. The percentage of wood failure in the bonding area for each specimen was assessed visually.

RESULTS AND DISCUSSION

Resin characterization

The pH value, nonvolatile content, viscosity, free formaldehyde level, and free phenol remaining of all the resins were measured and are presented in Table I. The pH values of all of the resins ranged from 9.5 to 10.5. The nonvolatile contents of all of the biobased resins were very close and were slightly higher than that of the pure PF resin. The lower nonvolatile content of the pure PF resins might have been caused by the low molar ratio of formaldehyde to phenol of 1.3 used during the synthesis; this resulted in excessive phenol (6.2 wt %, as shown in Table I), which was not consumed with formaldehyde in the reaction. The unreacted phenol evapo-

rated during the heating period, and this led to a lower nonvolatile content for the pure PF resin. As expected, the free phenol remaining in the BPF resol resins was much lower, for example, less than 0.1 wt % in 50% BPF (Table I). A possible explanation is that phenol is more reactive with formaldehyde than bio-oil, which results in much lower free phenols in the BPFs. The viscosities of the BPFs increased with increasing bio-oil ratio, most likely because of the much larger molecular weights and complex molecular structures of the biophenolic compounds in the bio-oil compared to those of phenol.[17] A free formaldehyde content was not detected for the pure PF resin, whereas it was detected in all of the BPF resins, and the content increased with increasing bio-oil ratio; this suggested a lower reactivity of bio-oil over phenol.

DSC thermograms were obtained under dynamic conditions at different heating rates (5, 10, 15, and 20°C/min) to study the kinetics of the curing reactions. The DSC profiles of various BPF and PF resol resins at 10°C/min are displayed in Figure 1. The DSC thermograms of all of the BPF resins exhibited an exothermic peak between 145 and 155°C, depending on the amount of bio-oil present in the formula. The main exothermic peak was generally attributed to the condensation of phenol or bio-oil with methylol groups ($-CH_2OH$) to form a methylene
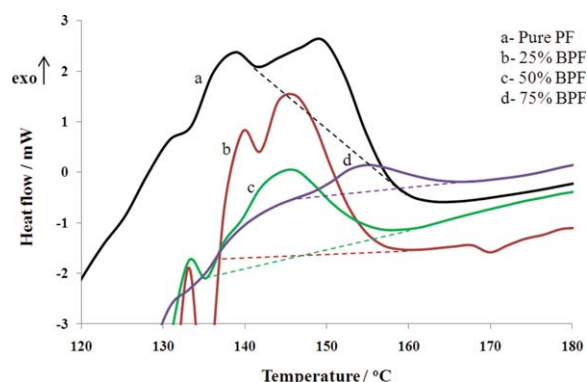

Figure 1 DSC profiles of various BPF and PF resol resins at 10°C/min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE II
DSC Results of the Main Exothermic Peak of the BPF and PF Resol Resins at a Heating Rate of 10°C/min

	Type of resol resins			
	PF resin	25% BPF	50% BPF	75% BPF
Onset temperature (°C)	142.3	136.6	135.2	148.3
T_p (°C)	149.5	145.4	145.5	154.8
End temperature (°C)	162.6	156.9	156.9	165.7

bridge and the condensation of two methylol groups to form dibenzyl ether bridges.[19–21] The DSC profiles of the BPFs also displayed shoulder peaks between 130 and 140°C, which might have been caused by the addition of free formaldehyde (as detected and shown in Table I) to form phenolic rings.[19,21,22] As shown in Figure 1, the pure PF resin exhibited two distinct peaks at 140 and 150°C. The first peak was attributed to the condensation to form methylene and dibenzyl ether bridges, and the second peak at the higher temperature might have been related to the subsequent reactions, for example, the breakage of dimethylene ether linkages and recondensation through the methylene bridges.[20,21,23] The DSC results of the main exothermic peak of the BPF and PF resol resins at a heating rate of 10°C/min are summarized and displayed in Table II. Interestingly, from Table II, at a low bio-oil ratio of 50 wt % or lower, the curing temperatures were lower than those of the pure PF resin. This result suggests that the presence of bio-oil promoted the curing reactions of the BPFs; this was consistent with reported previously results,[21,23,24] where the addition of a small amount of biophenol materials in the PF resin (e.g., tannin and lignin) reduced the curing temperature. The resins containing bio-oil more than 50 wt % (i.e., the 75 wt % BPF), however, displayed a higher curing temperature than the pure PF resin, as we observed previously.[21] These results suggest that the presence of bio-oil in a BPF resin could play two adverse roles in the process of curing, depending on the amount of bio-oil in the BPF resins. For a BPF resin with a low bio-oil ratio, a small amount of bio-oil would favor the thermal curing reaction, governed by phenol. For a BPF resin with a high bio-oil ratio, the bio-oil becomes the majority component in the resin, and the thermal curing reactions are retarded by the low reactivity of bio-oil.

Nonisothermal DSC scanning methods have been widely used to investigate the curing kinetics of thermosetting phenolic resins.[20,21,25,26] Because the results from a single heating rate may be inconsistent,[23,26] a multiple-heating rate method was used with four different heating rates from 5 to 20°C/min. Assuming that the curing reaction pathway did not change with the heating rate, we calculated the curing kinetic parameters of the curing reaction of the resins with the Kissinger and Crane equations:[27,28]

$$\text{Kissinger equation:} \quad \frac{d\ln\left(\beta/T_p^2\right)}{d\ln\left(1/T_p\right)} = -\frac{E}{R} \quad (1)$$

$$\text{Crane equation:} \quad \frac{d\ln\beta}{d\left(1/T_p\right)} = -\frac{E}{nR} \quad (2)$$

where β is the heating rate (°C/min), T_p is the maximum exothermic or peak temperature (T_p) in the DSC profile (K), E is the activation energy (kJ/mol), and R is the gas constant (= 8.314 J//mol/K). E and the reaction order (n) were calculated from the slope of the regression line of plots of $\ln(\beta/T_p^2)$ and $\ln\beta$ versus $1/T_p$, respectively. The working plots are displayed in Figure 2, and the calculated results are listed in Table III. The curing reaction for all of the resol resins was approximately first order ($n = 0.94$–0.95), as observed previously.[21] The value of E was the lowest for 25% BPF but increased with increasing bio-oil ratio in the BPF resins. As indicated in Table III, the E values of all of the BPFs were lower than that of the pure PF resin; this might be explained by two reasons. First, the bio-oil contained
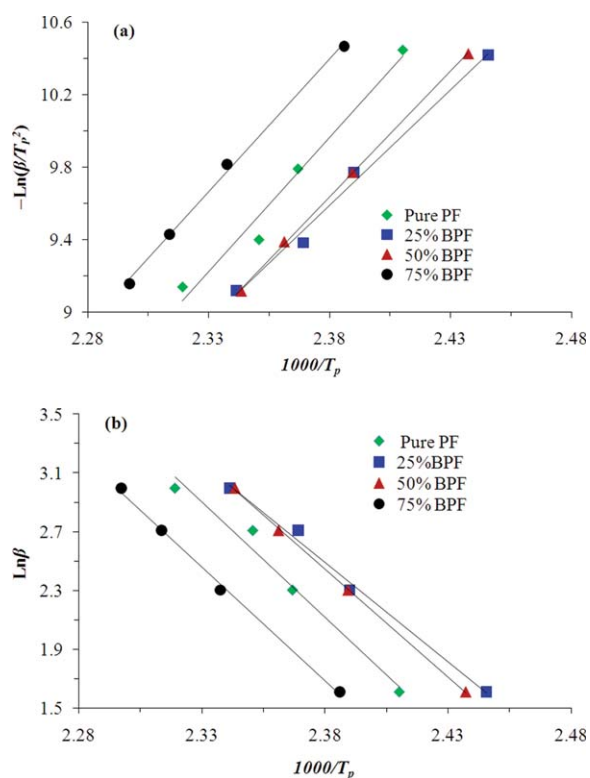

Figure 2 Plots of DSC kinetic analysis by the (a) Kissinger and (b) Crane equations. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

| Type of resol resins | DSC results | | Curing characteristic T_p at 0°C/min (°C)[a] | E (kJ/mol)[b] | n[c] |
	Heating flow (°C/min)	T_p (°C)			
Pure PF	5	141.9	138.1	123.2	0.95
	10	149.5			
	15	152.4			
	20	158.2			
25% BPF	5	135.9	131.6	105.9	0.94
	10	145.4			
	15	149.1			
	20	154.1			
50% BPF	5	137.3	133.2	115.3	0.94
	10	145.5			
	15	150.5			
	20	153.7			
75% BPF	5	146.1	142.4	122.0	0.95
	10	154.8			
	15	159.2			
	20	162.3			

[a] By linear extrapolation.
[b] Based on the Kissinger equation.
[c] Based on the Crane equation.

lignin-derived oligomers that were readily to cross-link and cure. Second, the addition of a small amount of bio-oil in the PF resins could have promoted the curing reaction more, as the bio-oil could act as a high efficient crosslinking reagent (with multiple unoccupied reactive sites on the bio-oil molecules).[21,29] However, at high bio-oil ratios in the BPFs (>50 wt %), the curing E increased because of the lower reactivity of bio-oil compared to that of phenol.

The thermal stability of the nonvolatile contents of the BPF and PF resol resins were also evaluated by TGA. Figure 3 contains the thermogravimetry (TG)–differential thermogravimetry (DTG) results of the resol resins between 25 and 700°C. The decomposition temperatures, mass loss values of the thermal events, and mass residue at 700°C are listed in Table IV. As shown in Figure 3, all of the BPFs and the PF resin represented similar thermal decomposition patterns and showed three major thermal events. It is known that the degradation of phenolic resins has three steps: postcuring, thermal reforming, and ring stripping.[30] The first event of the pure PF resin was observed in the range 70–300°C (6% mass loss), which could have been ascribed to the postcuring reactions of the resin (the removal of terminal groups and further crosslinking or condensation reactions). The second event was obtained from 365 to 500°C (5% mass loss), which could have been attributed to thermal reforming to break the bridged

methylene linkage. The last event was detected in the range 500–650°C (the main mass loss region, 11% mass loss) because of the breakdown of the ring network. When the ratio of bio-oil substitution in phenolic resol resins was lower than 50 wt %, the three decomposition ranges were 150–300°C (ca. 5% mass loss), 300–450°C (9% mass loss), and 450–650°C (the main mass loss region, 13% mass loss for 25% BPF and 23% mass loss for 50% BPF). The ranges of the thermal events of 75% BPF, however, were transferred to higher temperatures, that is, 150–300°C (7% mass loss), 300–600°C (the main loss region, 37% mass loss), and 600–700°C (8% mass loss). As discussed previously in the DSC analysis, the substitution of phenol with bio-oil at a ratio larger than 50 wt % would lead to a BPF resin whose properties were governed by the less reactive bio-oil. Thereby, the large mass loss (37%) for the 75% BPF 300–600°C was explained by the degradation of side chains present in the bio-oil molecules and the breakdown of the methylene linkage, as observed by Wang et al.[21] From the TG profiles, all of the bio-oil-derived resol resins possessed slightly superior thermal stability in terms of the residual carbon content below 240°C but became significantly inferior above this temperature, especially for the
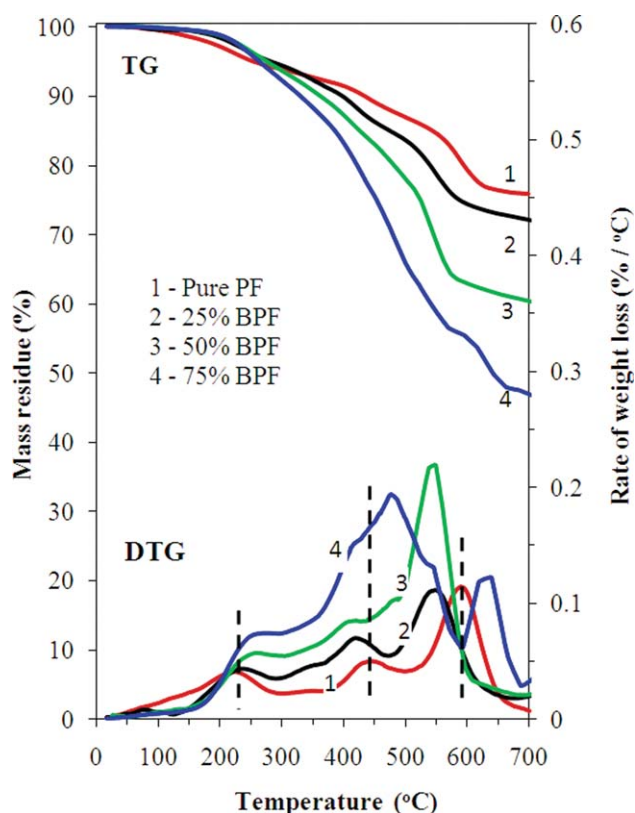

Figure 3 TG and DTG profiles of the BPF and PF resol resins. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE IV
TG and DTG Results of the BPF and PF Resol Resins

	DTG results			TG results
Type of resol resins	First thermal event: $T_o/T_p/T_e$ (°C)[a]	Second thermal event: $T_o/T_p/T_e$ (°C)	Third thermal event: $T_o/T_p/T_e$ (°C)	Mass residue at 700°C (%)[b]
Pure PF	70/223/300 (6%)	365/445/500 (5%)	500/589/650 (11%)	76 (± 0.1)
25% BPF	150/236/300 (5%)	300/418/460 (9%)	460/548/650 (13%)	72 (± 0.05)
50% BPF	150/240/300 (6%)	300/393/430 (9%)	430/535/650 (23%)	61 (± 0.2)
75% BPF	150/240/300 (7%)	300/466/600 (37%)	600/616/680 (8%)	48 (± 0.9)

[a] T_o, onset temperature; T_e, endset temperature.
[b] An average of two samples.

BPFs with a high bio-oil ratio. As shown in Table IV, the residual carbon contents at 700°C were 76%, 72%, 61%, and 48% for the pure PF resin, the 25% BPF, the 50% BPF and the 75% BPF resins, respectively. The decrease in the carbon residue for a BPF resin at an increased bio-oil ratio was likely caused by the loss of numerous side chains from the bio-oil molecules. In summary, the BPF resins with up to 50 wt % bio-oil displayed a comparable thermal resistance to that of the pure PF resol resin.

Figure 4 shows the IR spectra of the BPF resins compared with that of the reference pure PF resin. All of the BPFs displayed similar IR absorption profiles to that of the pure PF resol; this indicated that the BPFs had similar chemical structures to the PF resol resins. All of the resins had typical hydroxyl group absorption between 3400 and 3387 cm^{-1}, C—H stretching between 2980 and 2875 cm^{-1}, and C—O stretching between 1000 and 1030 cm^{-1}. However, some difference were also observed among these spectra. For example, the signal between 1668 and 1715 cm^{-1} (attributed to the C=O stretching from ketone, aldehyde, and ester groups) became stronger for a BPF resin with a higher bio-oil content. This was accounted for by the high contents of ketone,

aldehyde, and ester groups in bio-oil, as reported in the previous research.[17] As expected, the characteristic peaks of the phenolic/aromatic structure[17,31] at 1605, 1500, 1450, 1248, 835, 758, and 694 cm^{-1} diminished with increasing bio-oil content in the BPFs.

The molecular weight distribution of all resol resins were obtained by the GPC chromatograms, as illustrated in Figure 5. The GPC profiles of all of BPFs displayed a broader molecular weight distribution than that of the reference PF resin and had higher M_w and M_n values. The values of M_w and M_n increased gradually with increasing bio-oil ratio in the BPFs; this could be explained by the large molecular weight of bio-oil and its broad molecular weight distribution (M_w = 1072 g/mol, M_n = 342 g/mol, polydispersity = 3.13).

Evaluation of the adhesive bonds

The tensile strengths (under both dry and wet conditions) of the plywood specimens prepared with various BPF and PF resol resins as adhesives were evaluated and are illustrated in Figure 6. Under dry
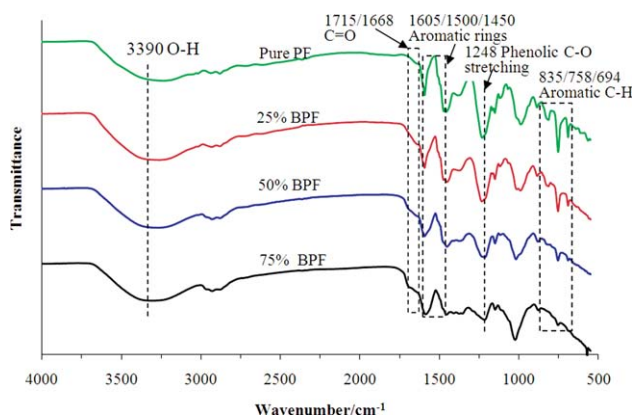
Figure 4 IR spectra of the various types of BPFs and the PF resol resin. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
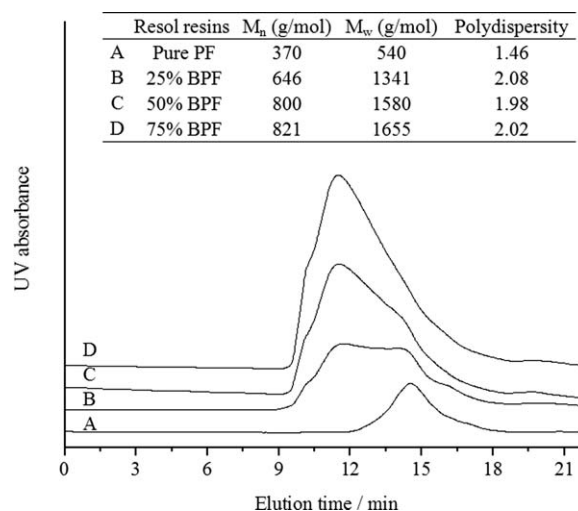
	Resol resins	M_n (g/mol)	M_w (g/mol)	Polydispersity
A	Pure PF	370	540	1.46
B	25% BPF	646	1341	2.08
C	50% BPF	800	1580	1.98
D	75% BPF	821	1655	2.02

Figure 5 GPC chromatograms of the acetylated BPF and PF resol resins (with THF as the eluent at 1 mL/min, UV detection at 270 nm, polystyrene standards).

conditions, the BPFs of with bio-oil ratios of up to 50 wt % performed better than the reference PF resin. For the 75% BPF, the dry tensile strength was lower than that of the 50% BPF, but it was still comparable to the reference PF resin. All of the BPFs surpassed the minimum requirement of the tension shear strength specified in the JIS K-6852 standard (i.e., 1.2 MPa) for resol-type adhesives. These results were superior to the results of previous studies where phenol was substituted with starch/tannin or Kraft lignin at a ratio of less than 50 wt %.[32,33] The addition of bio-oil to substitute for phenol at a high level (up to 75 wt%) still produced useful bio-based resol resins for plywood adhesives, likely because of the low molecular weights of the obtained phenolic bio-oil (M_w = 1072 g/mol, M_n = 342 g/mol). Under the wet conditions after boiling for 3 h, as expected, all of the specimens bonded with PF and BPFs gave a decreased tensile strength. Surprisingly, however, there was no significant difference among these resins, and all of the values exceeded the minimum value (1.0 MPa) of wet strength and even the minimum value of dry strength required in accordance with the same JIS standard mentioned previously. Table V presents the wood failure of both dry and wet plywood specimens bonded with PF and various BPFs after the tensile strength testing. The wood failure of the dry specimens displayed a similar trend as that observed for the dry tensile strength; that is, the specimens with BPF resol at bio-oil ratios up to 50 wt % produced a higher or similar wood failure than the pure PF resin-bonded specimen. All samples met the wood failure requirement (85%) for exterior-grade plywood. However, the wood failure decreased as the bio-oil ratio further increased from
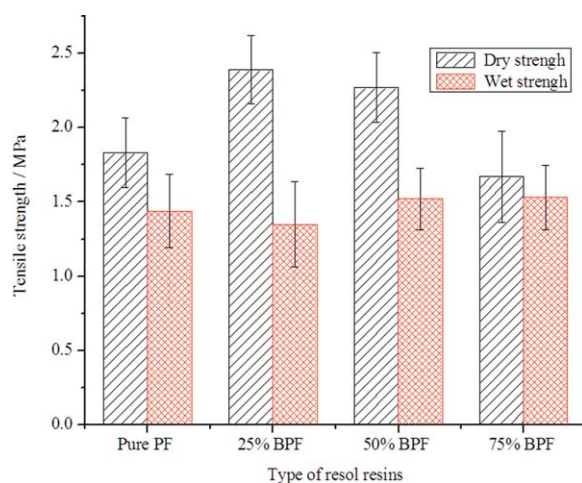
TABLE V
Wood Failure of the Plywood Samples Bonded with the BPF and PF Resol Resins

Test condition	Wood failure (%) ± standard deviation[a]			
	Pure PF	25% BPF	50% BPF	75% BPF
Dry[b]	89 ± 19	97 ± 13	87 ± 36	22 ± 33
Wet[c]	65 ± 43	33 ± 42	35 ± 41	15 ± 31

[a] From an average of 20 specimens.
[b] Test after conditioning.
[c] Test after boiling in water for 3 h.

50 to 75 wt % substitution. For example, the wood failure dropped from 87% (for the 50% BPF) to 22% (for the 75% BPF).

CONCLUSIONS

1. Phenolic bio-oil with a low molecular weight (M_w = 1072 g/mol, M_n = 342 g/mol) produced from the direct liquefaction of Eastern white pine (*P. strobus L.*) sawdust in a hot-compressed ethanol–water (1 : 1 wt/wt) medium at 300°C was successfully used to partially substitute for phenol at a high substitution level (up to 75 wt %) in the synthesis of BPF resol resins.

2. All of the BPFs displayed similar physical/chemical properties (nonvolatile content, pH value, IR adsorption, etc.) to the reference pure PF resol resin, whereas the viscosities, free formaldehyde levels, and molecular weights of the BPFs were all greater than those of the pure PF resin, as was expected.

3. All of the BPFs were curable at a temperature of 130–160°C. The resins containing bio-oil contents of greater than 50 wt % (i.e., the 75 wt % BPF) displayed a higher curing temperature than the pure PF resin. At a low bio-oil ratio (≤50 wt %), however, the curing temperatures were lower than that of the pure PF resin; this suggested that the presence of bio-oil promoted the curing reactions of the BPFs. The curing reaction for all of the resol resins proved to be approximately first order, and the E values of all of the BPFs were lower than that of the pure PF resin.

4. The residual carbon contents at 700°C for the BPFs (25–75 wt % bio-oil ratios) were in the range 72–48%.

5. The addition of bio-oil to substitute for phenol at a high level (up to 75 wt%) produced useful bio-based resol resins for plywood adhesives and had comparable or better dry/wet bonding strength than the reference pure PF resin.

Figure 6 Tensile strength of the plywood samples bonded with the BPF and PF resol resins (dry strength: test after conditioning, wet strength: test after boiling in water for 3 h). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

References

1. Gani, A.; Naruse, I. Renew Energy 2007, 32, 649.
2. Bridgwater, A. V.; Peacocke, G. V. C. Sustainable Renew Energy Rev 2000, 4, 1.
3. Sánchez, C. Biotechnol Adv 2009, 27, 185.
4. Harkin, J. M.; Rowe, J. W. USDA Forest Service Research Note FPL-091 Bark and its possible uses. Revised 1971. Available on at http://www.fpl.fs.fed.us/documnts/fplrn/fplrn091.pdf. Access date: January 2, 2011.
5. Kleinert, M.; Gasson, J. R.; Barth, T. J Anal Appl Pyrolysis 2009, 85, 108.
6. Wang, M.; Xu, C.; Leitch, M. Bioresour Technol 2009, 100, 2305.
7. Liu, Z.; Zhang, F. Energy Convers Manage 2008, 49, 3498.
8. Bridgwater, A. V. Thermal Science 2004, 8, 21.
9. Amen-Chen, C.; Riedl, B.; Wang, X. M.; Roy, C. Holzforschung 2002, 56, 281.
10. Zhang, Q.; Zhao, G.; Chen, J. Front For China 2006, 2, 214.
11. Roy, C.; Liu, X.; Pakdel, H. 2000. US Patent 6 143 856, Pyrovac Technologies Inc. Access date: January 2, 2011.
12. Lee, S. H. J Appl Polym Sci 2003, 87, 1365.
13. Russell, J. A.; Riemath, W. F. (to U.S. Department of Energy). U.S. Pat. 4,508,886 (1985).
14. Alma, M. H.; Maldas, D.; Shiraishi, N. J Polym Eng 1997, 18, 163.
15. Alma, M. H.; Basturk, M. A.; Shiraishi, N. Ind Eng Chem Res 2001, 40, 5036.
16. Effendi, A.; Gerhauser, H.; Bridgwater, A. V. Renew Sustain Energy Rev 2008, 12, 2092.
17. Cheng, S.; D'Cruz, I.; Wang, M.; Leitch, M.; Xu, C. Energy Fuels 2010, 24, 4659.
18. Walker, J. F. Formaldehyde; Krieger: Huntington, NY, 1975; p 493.
19. Christiansen, A. W.; Gollob, L. J Appl Polym Sci 2003, 6, 2279.
20. Gabilondo, N.; López, M.; Ramos, J. A.; Echeverría, J. M.; Mondragon, I. J Therm Anal Calorim 2007, 1, 229.
21. Wang, M.; Leitch, M.; Xu, C. Eur Polym J 2009, 12, 3380.
22. Alonso, M. V.; Oliet, M.; Pérez, J. M.; Rodríguez, F.; Echeverŕ, J. Thermochim Acta 2004, 419, 161.
23. Vázquez, G.; González-Álvarez, J.; López-Suevos, F.; Freire, S.; Antorrena, G. J Therm Anal Calorim 2002, 70, 19.
24. Khan, M. A.; Ashraf, S. M.; Malhotra, V. P. J Appl Polym Sci 2004, 92, 3514.
25. Wang, M.; Wei, L.; Zhao, T. Eur Polym J 2005, 41, 903.
26. Park, B.; Riedl, B.; Hsu, E. W.; Shields, J. Polymer 1999, 40, 1689.
27. Kissinger, H. E. Annu Chem 1957, 29, 1702.
28. Crane, L. W.; Dynes, P. J.; Kaelble, D. H. J Polym Sci Polym Lett Ed 1973, 11, 533.
29. Tymchyshyn, M.; Xu, C. Bioresour Technol 2009, 7, 2483.
30. Khan, M. A.; Ashraf, S. M. J Therm Anal Calorim 2007, 89, 993.
31. Serrano, V. G.; Villegas, J. P.; Florindo, A. P.; Valle, C. D.; Calahorro, C. V. J Anal Appl Pyrolysis 1996, 36, 71.
32. Moubarik, A.; Pizzi, A.; Allal, A.; Charrier, F.; Charrier, B. Ind Crops Prod 2009, 30, 188.
33. Danielson, B.; Simonson, R. J Adhes Sci Technol 1998, 12, 923.