

Bio-oil from Whole-Tree Feedstock in Resol-Type Phenolic Resins

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ABSTRACT: Renewable chemicals are of growing importance in terms of opportunities for environmental concerns over fossil-based chemicals. Lignocellulosic biomass can be converted into energy and chemicals via thermal and biological processes. Among all the transformation processes available, fast pyrolysis is the only one to produce a high yield of a liquid-phase product called bio-oil or pyrolysis oil. Bio-oil is considered to be a promising substitute for phenol in phenol formaldehyde (PF) resin synthesis. In this work, bio-based phenolic resins have been formulated, partially substituting phenol by bio-oils from two Canadian whole-tree species. The new resins are produced by replacing 25, 50, and 75% of phenol with bio-oil for each species (three bioresins per species). The aim of this study is to synthesize renewable resins with competitive price and satisfactory quality. The results obtained have shown that substitution degree up to 50% provided reactivity and performance equal or superior to the pure PF resin. They also present a good storage stability, improved shear strength, and thermal stability comparable to the pure PF. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2014, 131, 40014.

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INTRODUCTION

Phenolic resins are known as the oldest thermosetting polymers produced by the condensation of petroleum-based phenol with formaldehyde. They are widely used in many industrial applications in sectors such as automotive, computing, aerospace, and building^{1,2} because of their resistance to high temperatures and flame, electrical insulation, and dimensional stability. They are also used as wood adhesives in the manufacturing of engineered wood products, such as plywood, laminates veneer lumber, particleboard, and oriented strand board.³ It is recognized that the composite wood panels bonded with phenol formaldehyde (PF) adhesives emit almost no formaldehyde.^{4,5}

Because of the scarcity of fossil feedstock, the rising price of petroleum-based products, and the environmental concerns over fossil fuels, lignocellulosic biomass represents a sustainable alternative as a feedstock for chemical. Lignocellulosic biomass can be converted into organic compounds, including phenolic compounds, by thermochemical technologies, such as pyrolysis and liquefaction.^{6–11} In the last decade, researchers have made much effort to partially replace petrochemical phenol by phenolics from renewable resource such as lignins, tannins, cardanol, bio-oil, and biocrude.^{1,12–16}

Fast pyrolysis is an efficient thermochemical technology for conversion of woody biomass. The products of pyrolysis are

bio-oil, biochar, and non-condensable gases with yields of 55–65, 25–30, and 10–15%, respectively. Bio-oil is a good candidate as phenol substitute, whereas biochar and non-condensable gases can be injected into the system to heat the pyrolysis reactor. Biochar is particularly used as soil amendment. During pyrolysis, lignocellulosic biomass undergoes hydrolysis, degradation, and decomposition reactions to become small fragments or mono-molecular compounds. Bio-oil is rich in phenolic compounds mainly found in the form of oligomers, also called pyrolytic lignin. In addition to the phenolic fraction, there are effectively other compounds like sugars, alcohols, aldehydes ketones, and organic acids. It also contains 20–30% water. Considerable research has been performed to use pyrolysis oils for the preparation of PF resins.^{17–20} However, to our knowledge, no information is available on the use of bio-oil produced from whole-tree feedstock, and particularly from Canadian species, for the production of PF-type adhesives. In Bas-Saint-Laurent region (Quebec, Canada), there is increasing concern about the excess inventory of small-diameter trees that need to be thinned to improve forest health. Approximately, 300,000–450,000 m³/ha/yr of the trees can be removed during a commercial thinning until 2036. Often considered as nonusable or underutilized timbers, fast pyrolysis for the production of chemicals and fuels can be a way to ensure viable markets for the removed material.

Table I. Cell Wall Composition of the Two Feedstocks

	Feedstock	
	Trembling aspen	White spruce
Cell wall composition ^a (dry basis)		
KH cellulose (%)	52.2	53.6
Hemicelluloses (%)	23.4	16.8
Lignin (%)	24.4	29.6
Elemental analysis (dry basis)		
C (%)	49.85	49.67
H (%)	6.17	6.04
N (%)	0.26	0.10
O (%)	43.73	44.19
Proximate analysis (dry basis)		
Humidity (%)	5.3	6.0
Volatile matter (%)	78.6	77.1
Ash (%)	1.3	0.8
Fixed carbon (%)	14.9	16.1

^aThe main cell wall compositions were determined in accordance with the Kürschner and Hoffner nitric acid method for cellulose and with ASTM D1106 standard method for lignin. Hemicellulose content was determined by difference.

In this study, bio-oils produced by the fast pyrolysis of two Canadian small-diameter whole-tree feedstocks (white spruce and trembling aspen) were used to partially substitute petroleum-based phenol for the synthesis of bio-oil phenol formaldehyde (BO-PF) resins. Prepared adhesives were characterized in detail and compared with PF adhesive in performance.

EXPERIMENTAL

Materials

Small-diameter trees (8–10 cm in diameter) of trembling aspen (*Populus tremuloides*) and white spruce (*Picea glauca*) were collected from the Groupe BSL sawmill located in Amqui, Quebec, Canada. The whole-tree feedstocks (without debarking) were chipped directly onsite using a disk chipper to 1.58 cm [5/8 inch] along the grain and oven-dried to 8% moisture contents. The detailed analysis results of the two feedstocks, including proximate and ultimate analyses and cell-wall compositions, are presented in Table I. The pyrolysis experiments were performed in a reactor Auger, which is heated electrically at the desired temperature of pyrolysis. The dried feedstock (ca. 0.5–2 mm) is introduced with an Auger screw into a stainless steel tube (length of 65 cm and diameter of 10 cm) at a feeding rate of 1.5 kg/h. Nitrogen was used as carrier gas at a flow rate of 5 L/min. Pyrolysis vapor is collected by a series of two condensers. The first unit was a vertical tube with cooling coils cooled with ambient water. The second condensation unit consisted of a system cooled to -10°C . The bio-oils used in this study as a phenol substitute were obtained from feedstock by fast pyrolysis in a Labscale Auger reactor at 500 and 400°C , respectively, for white spruce and for trembling aspen, which temperatures cor-

respond to the optimized yields of bio-oil for each feedstock (55–65% on a dry basis, not published data). The solvents and chemicals used in this study were distilled water, ACS reagent-grade ethanol (ca. anhydrous, Les alcools de commerce, Boucherville, QC), liquefied phenol (ca. 90%, Laboratoire Mat, Quebec, QC), sodium hydroxide (Laboratoire Mat), and formaldehyde (ca. 37%, Laboratoire Mat).

Synthesis of PF and BO-PF Resol Resins

BO-PF and PF resins with formaldehyde to phenol (F/P) ratio of 1.3/1.0 were prepared according to the method described by Cheng et al.³ with a slight modification. Bio-oils from the two feedstocks were added in several concentrations (25, 50, and 75% wt) in total amount of phenol used in synthesis of BO-PF. A total of six bio-oil PF resol resins, three per species, has been synthesized in this study. The optimum conditions for the formulation BO-PF resins were obtained after several experiments (not published data). In brief, phenol, bio-oil, ethanol, and sodium hydroxide solution (ca. 33% wt) were loaded in different proportions into a kettle equipped with a mechanical stirrer and a reflux condenser. The mixture was heated to 60°C and maintained at this temperature for 1 h under stirring. After homogenization of the mixture, the temperature was raised to 80°C and formaldehyde solution was added drop-wise over a period of 10 min. The reaction mixture was then heated to 95°C and kept at this temperature until the viscosity of the resin reached between 180 and 300 cP. This range of viscosity has been target to synthesize resol resins suitable for particle-board manufacturing. The synthesis procedure used to prepare the resins is summarized in Table II.

Physical Properties

The pH values of the resins were measured at $25 \pm 2^{\circ}\text{C}$. The viscosity of all the phenolic resins was measured at $25 \pm 2^{\circ}\text{C}$ using a Brookfield rotary viscometer with a spindle SC4–31 according to ASTM D1084-08. The non-volatile contents of the obtained resins were determined in accordance with ASTM standard D4426-06. Gel times were measured at $120 \pm 1^{\circ}\text{C}$.

Free Formaldehyde Level

The free formaldehyde levels in the resins were determined in accordance to ISO 11402. Approximately 2 g of resin was diluted with 25 mL of methanol, and the pH was adjusted to 4.0 with 0.5M HCl. Thirty milliliter 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 0.5M aqueous sodium hydroxide.

Shelf Life

Storage life of PF and BO-PF resins was studied according to ASTM D1337-10. Shelf life was measured by determining the viscosity of the freshly prepared and stored adhesives. The adhesives were stored in sealed polyvinyl chloride tubes at $25 \pm 2^{\circ}\text{C}$. The viscosity was measured weekly for 5 weeks to check the shelf life of the adhesives.

Thermomechanical Analysis

The thermal cure properties of the resins were evaluated with a thermomechanical analysis (TMA) (TMA 40, Mettler-Toledo,

Table II. Resin Synthesis and Reagent Molar Ratio Used

Species	% wt of bio-oil/phenol	Resin code	F/P molar ratio	NaOH/P molar ratio	EtOH/P molar ratio	Time to reach 180–300 cP (h)
NA ^a	0	PF	1.3	0.2	0.2	1.0
Trembling aspen	25	TA-Bio25-PF	1.3	0.7	0.2	1.5
Trembling aspen	50	TA-Bio50-PF	1.3	0.7	0.3	1.75
Trembling aspen	75	TA-Bio75-PF	1.3	0.7	0.3	1.0
White spruce	25	WS-Bio25-PF	1.3	0.7	0.2	1.75
White spruce	50	WS-Bio50-PF	1.3	0.7	0.3	2.0
White spruce	75	WS-Bio75-PF	1.3	0.7	0.3	1.25

^aNA, Not available.

Switzerland) and STARe data processing software. The experiments were performed from 30 to 250°C under 50 mL/min N₂ with a heating rate of 10°C/min, using 30 mg of resin between two birchwood plies of dimensions 21 × 6 × 0.7 mm. The experiments were performed in TMA three points bending mode with a fixed periodic force of 0.01/0.05 N automatically applied to the sample. From the rigidity development curves, the cure time and modulus of elasticity (MOE) are determined. The MOE of a wood-resin system gives a good indication of the end strength of the final application of the glue tested.

Thermogravimetric Analysis

The thermal stability of the cured resins was determined by thermogravimetric analysis (TGA) (TGA, Perkin-Elmer Pyris STA 6000) from 35 to 700°C. The non-volatile resin sample (10 mg) was heated in an Al pan at a heating rate of 10°C/min under a nitrogen atmosphere with a flow rate of 30 mL/min. Curves of weight loss and derivative weight loss (DTG) were plotted.

Strength Properties of PF and BO-PF Adhesive Bonds

The shear bonding strength test was performed according to the standard D905-08. Blocks of maple conditioned at 10–12% MC were used for sample preparation. Blocks were glued using different formulations of resins. The glue spread applied is 200 g/m², and the blocks were hot pressed at 120°C for 20 min at a pressure of 1.0 MPa. The samples (five for each condition) were stored at 20 ± 1°C and 65 ± 2% relative humidity before testing to get 10–12% MC. The dimensions of the samples and test methods were based on the standard D905-08. The samples were tested for shear stress by compression to failure with an Instron Bench-top universal testing machine with 5 mm/min loading speed.

RESULTS AND DISCUSSION

PF and BO-PF Resins

Table II presents the different resin formulations and the reagent molar ratios used in this study. One can observe that 1 h was necessary to achieve final viscosity between 180 and 300 cP for PF, whereas a longer time was required for BO-PF resins except for TA-BO75-PF. This could be the result of the presence of certain larger molecular compounds. Phenolic compounds

issued from fast pyrolysis of lignin feedstocks are mainly found in bio-oil as a form of oligomers called pyrolytic lignin,²¹ which are less reactive than phenol toward formaldehyde because of their steric hindrance. Complex phenolic compounds from lignin decomposition can have molecular weights as high as 5000 amu.¹¹ In addition, the presence of non-phenolic compounds derived from carbohydrate makes the bio-oil less reactive than petrochemical-based phenol. In general, for the same % wt substitution of bio-oil to phenol, it required more time to synthesize the BO-PF resins originated from white spruce bio-oil than those from trembling aspen. This can be explained by the weight-average molecular weight (M_w) of softwood pyrolytic lignin, which has been reported to be larger than that of hardwoods.¹¹ Softwood pyrolytic lignins have a larger tendency to polymerize, because unsubstituted positions ortho to the phenol hydroxyl exist in softwood lignins.

Physical Properties of PF and BO-PF Resins Prepared

Viscosity, pH value, non-volatile content, gel time, free formaldehyde level, and shear bonding strength of all resins were determined and are presented in Table III. BO-PF resins have slightly lower solid contents (ranging from 42.1 to 47.8%) than PF resin that may be justified by the high water content in the bio-oils (approximately 30% wt). They also have a relatively high pH compared with the PF resin in relation with NaOH/P ratio used for the BO-PF resins synthesis (0.7/1). More NaOH is required for BO-PF resins, partly due to high acidity of bio-oils (pH 2–3). BO-PF resins have a gel time higher than PF, indicating that more time will be needed to cure. At the same substitution level, gel time of white spruce bio-oil phenol formaldehyde (WS-BO-PF) resins is higher than that of trembling aspen bio-oil phenol formaldehyde (TA-BO-PF) resins. This result confirms the difference between the chemical nature of white spruce and trembling aspen bio-oils, in term of pyrolytic lignin molecular weight. Larger molecular weight pyrolytic lignins expected for white spruce feedstock cure lower than that of trembling aspen. However, one can observe that the better compromise in term of gel time is BO50-PF for both species. Free formaldehyde is not detected for the PF resin. However, it is detected in all BO-PF resins and its level increases with increasing % wt substitution level suggesting low reactivity of bio-oil compared with phenol

Table III. Properties of Formulated Resins

Resin code	Final pH at 23°C ^a	Final viscosity at 25°C (cP) ^a	Solid content (%) ^a	Gel time (sec) ^a	Free formaldehyde levels (%) ^a	Shear strength (MPa) ^b
PF	10.5	233	49.2	315	ND ^c	19.03 ± 2.15
TA-Bio25-PF	12.1	203	46.4	390	0.07	23.15 ± 1.90
TA-Bio50-PF	12.0	224	45.4	330	0.29	20.48 ± 0.80
TA-Bio75-PF	10.4	250	42.1	570	0.50	13.27 ± 1.33
WS-Bio25-PF	12.1	189	47.8	435	0.07	21.28 ± 1.30
WS-Bio50-PF	12.2	187	45.9	390	0.37	22.08 ± 0.99
WS-Bio75-PF	11.1	210	45.0	540	0.51	11.11 ± 2.00

^aEach value represents an average from two samples.

^bEach value represents an average from five samples.

^cND, not detectable.

due to less free position in the aromatic rings or an excess of formaldehyde.

Shelf Life

Shelf life of the different adhesives (PF and BO-PF) was studied according to ASTM standard D1337-10 by following their viscosities for 4 weeks. Figure 1 gives the viscosity of the resins according to the storage time. For all resins tested, the initial viscosity was around 200 cP. Beyond the first week, an increase of viscosity was observed. The study shows that viscosity of PF and BO-PF adhesives increases continuously throughout the storage period. Viscosities of BO25-PF and BO50-PF for both feedstock increase more slowly than PF throughout the storage period. In contrast, at 75% wt substitution level, the resin viscosities increase drastically in the second and the third week, respectively, for TA-BO75-PF and WS-BO75-PF, reaching a

viscosity greater than that required for the manufacture of particleboards. When comparing the origin of the bio-oil, the shelf life tests suggest that TA-BO-PF resins are more reactive than WS-BO-PF resins, in accordance with the gel time finding.

TMA of PF and BO-PF Resins

MOE curves of the different resin formulations obtained by TMA are shown in Figure 2. It seems that the addition of bio-oil up to 50% in resin formulations (TA-BO25-PF, TA-BO50-PF, WS-BO25-PF, and WS-BO50-PF) leads to a much tighter cross-linked network than PF resins. In contrast, at 75% wt substitution level (TA-BO75-PF and WS-BO75-PF), it seems that bio-oil may act like a filler, leading to a loose resin-hardened network. This can be explained by the increase of larger molecular weight compounds loading in the resin formulations. Zhao et al²² found that the curing of a PF adhesive can be followed

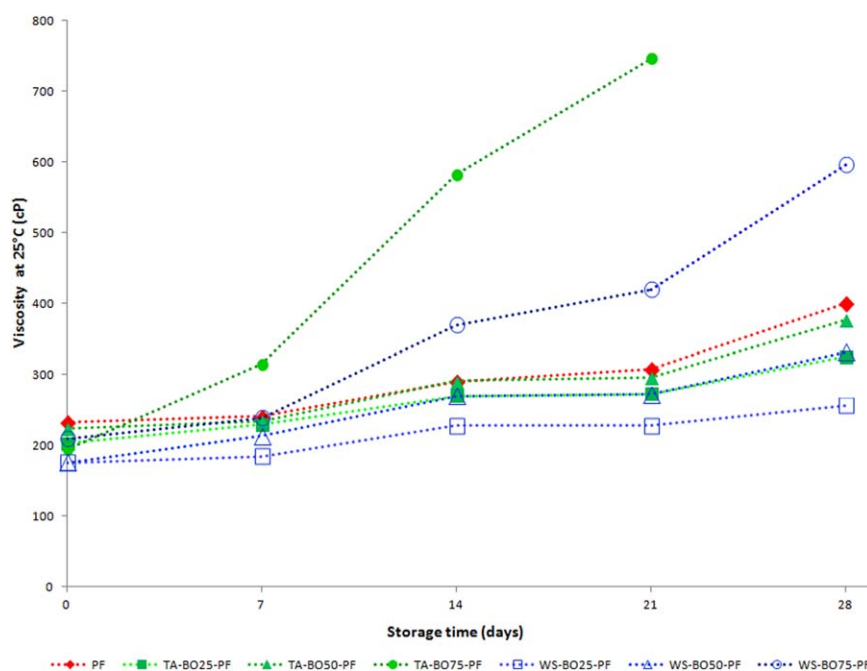


Figure 1. Effect of storage time on PF and BO-PF resin viscosities. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

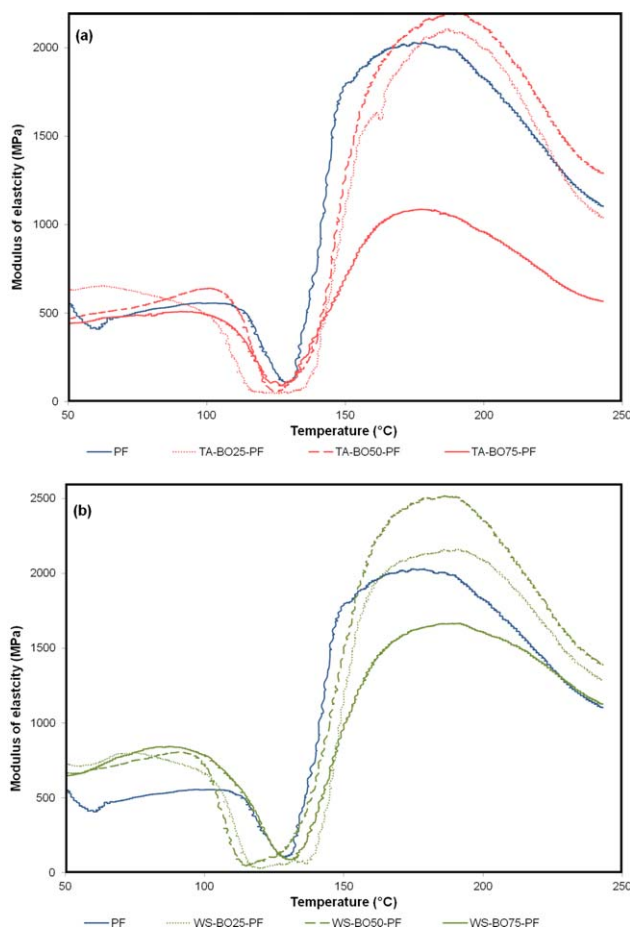


Figure 2. Thermomechanical analysis of the hardening of PF and BO-PF resins *in situ* in a wood joint: (a) bio-oil/PF resins from trembling aspen; (b) bio-oil/PF resins from white spruce. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

in situ in the wood joint itself, by TMA bending experiments and the results obtained can give the optimal results of internal bonds (IB) of particleboard pressed under standard conditions of press time and density. Our results suggest that particleboards glued with the four BO-PF resins up to 50% wt substitution level might have better IB strength than with conventional PF resins. All BO-PF resin MOE curves shift to higher temperatures compared with PF resin; hence, suggesting later reaction times and higher gel temperature. This may result in the extension of the pressing time of BO-PF resins when manufacturing particleboards.

TGA Thermodegradation of Cured Resins

Thermal stability of cured PF and BO-PF was evaluated by TGA. Figure 3 shows the TGA and DTG curves of the different cured resins obtained with bio-oil from trembling aspen and white spruce. Decomposition temperatures, values of mass loss for thermal events, and the residual carbon at 700°C are given in Table IV. It is reported that PF resin degrades in three major thermal events: postcuring, thermal reforming, and ring stripping.^{16,23} All BO-PF resins show similar thermal decomposition patterns as PF resins. One can observe in Figure 3 that PF resin has better thermal stability than BO-PF resins. Regardless of the

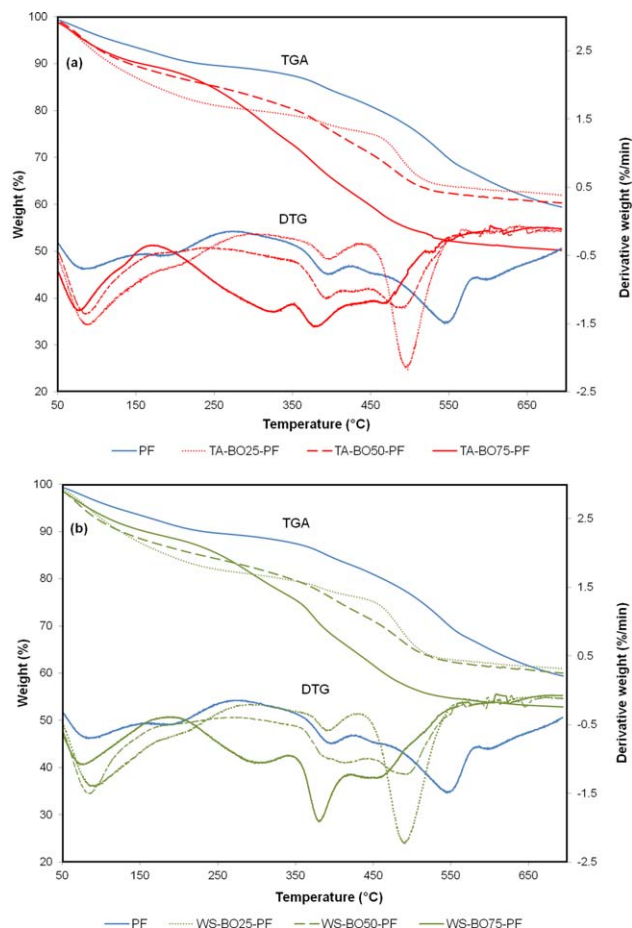


Figure 3. TGA and DTG curves of PF and BO-PF resins: (a) bio-oil/PF resins from trembling aspen; (b) bio-oil/PF resins from white spruce. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

feedstock, BO-PF resins with substitution level of bio-oil to phenol up to 50% present the same range of temperature in term of thermal events (Table IV). However, the ranges of thermal events for BO75-PF resins are shifted to lower temperatures. High substitution level of bio-oil to phenol (ca. 75% wt) may lead to weak cross-linked networks, which may affect the thermal stability of the cured BO75-PF resins. These results are in accordance with the TMA results obtained in this study. The lower thermal stability of BO75-PF resins can also be explained by the degradation of side chains present in the molecules of bio-oil and by breakdown of methylene linkage.^{3,24} This is confirmed by the decrease of the residual carbon content with increasing bio-oil substitution level due to the loss of many side chains from bio-oil compounds.

Strength Properties of PF and BO-PF Adhesive Bonds

ASTM D905 standard method is commonly used to evaluate the strength properties of adhesive bonds for qualifying the formulated resins. The shear strength of maple samples glued with the different resins formulated in this study was evaluated and shown in Table III. Pure PF resin has bond strength of 19.03 MPa. All BO-PF resins with bio-oil ratios up to 50% wt yield better or equivalent results than the pure PF. For BO75-PF

Table IV. TG and DTG Results of the BO-PF and PF Resins

Resin code	DTG results ^a			TG results ^a
	1st thermal event $T_O/T_p/T_e$ (°C) ^b	2nd thermal event $T_O/T_p/T_e$ (°C)	3rd thermal event $T_O/T_p/T_e$ (°C)	Residue at 700°C (%)
PF	35/80/300 (11%)	300/380/425 (6%)	425/537/580 (17%)	58.42 (± 1.45)
TA-Bio25-PF	35/85/300 (20%)	300/395/435 (4%)	435/490/580 (14%)	62.73 (± 0.38)
TA-Bio50-PF	35/85/300 (17%)	300/390/435 (10%)	435/485/580 (11%)	60.73 (± 0.59)
TA-Bio75-PF	35/75/185 (11%)	185/380/420 (26%)	420/470/580 (11%)	49.99 (± 0.20)
WS-Bio25-PF	35/85/300 (19%)	300/385/435 (5%)	435/490/580 (14%)	61.36 (± 0.57)
WS-Bio50-PF	35/85/300 (18%)	300/410/435 (9%)	435/490/580 (11%)	59.51 (± 0.62)
WS-Bio75-PF	35/75/185 (11%)	185/385/420 (23%)	420/455/580 (12%)	52.70 (± 0.17)

^aEach value represents an average from two samples.

^b T_O , onset temperature; T_p , peak temperature; T_e , endset temperature.

resins, and the shear strengths strongly decrease, confirming the TMA finding. One can observe that the nature of wood species (trembling aspen and white spruce) has no significant influence on the adhesion performance of the formulated BO-PF resins. The addition of bio-oil to substitute phenol in the formulation of PF-type resin up to 50% wt substitution level can produce bio-based resins as strong as conventional PF resins.

CONCLUSIONS

Crude bio-oils produced by fast pyrolysis of two Canadian small-diameter whole-tree feedstocks have been successfully used to partially replace phenol for the synthesis of bio-based PF resins without any pretreatment and fractionation. Physical and mechanical properties of BO-PF resins are strongly influenced by the substitution level of phenol. No significant differences between the resins formulated with trembling aspen and white spruce feedstock have been observed in this study. In summary, the bio-oil can be used as renewable phenol substitute at 50% wt substitution level in the synthesis of phenolic resins, which is able to improve certain properties of PF resole resins. It is also an economical and ecological alternative of conventional PF resole resins.

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