



Effects of bark extraction before liquefaction and liquid oil fractionation after liquefaction on bark-based phenol formaldehyde resoles



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ABSTRACT

Liquid product from white birch bark liquefaction in water/ethanol (50:50, v/v) mixture was successfully applied in substituting 50 wt% of phenol in the synthesis of bark based phenol formaldehyde (BPF) resole (i.e., 50% HTL-oil BPF resole). Besides, eHTL-oil from liquefaction of the bark extracted in 70 vol% aqueous acetone, and fHTL-oil obtained after HTL-oil fractionation in water, were also used to substitute 50% of phenol for BPF resoles synthesis. The results showed that all the three BPF resoles contained more free formaldehyde than the neat PF resole, and bark extraction before liquefaction and HTL-oil fractionation after liquefaction led to higher free formaldehyde contents in the resulted 50% eHTL-oil BPF resole and 50% fHTL-oil BPF resole. Furthermore, bark extraction before liquefaction retarded the curing of the resulted 50% eHTL-oil BPF resole, while HTL-oil fractionation after liquefaction slightly promoted the curing of the resulted 50% eHTL-oil BPF resole. All the three BPF resoles displayed less thermal stability than the neat PF resole, but the effects of bark extraction before liquefaction and HTL-oil fractionation after liquefaction on the thermal stability of the resulted BPF resoles were negligible. All the three BPF resoles could meet the bond strength requirements as adhesives for plywood in accordance to the JIS standard. Bark extraction before liquefaction led to less water resistance for the resulted 50% eHTL-oil BPF resole, while HTL-oil fractionation after liquefaction improved the water resistance of the resulted 50% fHTL-oil BPF resole.

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1. Introduction

Phenol formaldehyde (PF) resoles are the alkali catalyzed polycondensation products from phenol and formaldehyde with an F/P molar ratio >1.0. PF resoles have been widely used as adhesives for the manufacture of plywoods, oriented strand board (OSB), and particleboards, etc. Phenol as the most expensive raw material for PF resole is produced from non-renewable petroleum through the cumene hydroperoxide route in industry. Furthermore, phenol market is challenged by the declined reserves of petroleum resources. Thus, development of phenol alternatives from renew-

able resources has attracted increasing academic and industrial interests.

Bark refers to tree tissues external to the vascular cambium, which comprises 9–15% of a typical log by volume (USUD, 1971; Diamantopoulou, 2005). Compared with wood, bark is more abundant in lignin and tannins and can be converted into a phenol alternative via various thermochemical conversion processes such as pyrolysis, hydrothermal liquefaction, and more commonly phenolysis. In a typical phenolysis process, mixture of bark/phenol along with an acid catalyst are heated at 120–180 °C for hours. The slurry containing phenolated biomass, solid residue, free phenol, and acid is then filtered and rinsed by methanol. Methanol removal through evaporation results in a viscous liquid including phenolated biomass and free phenol, which can be directly used for PF resole synthesis. Bark species, catalysts, sodium hydroxide addition during PF resole synthesis would affect the properties of phenolated bark based PF resin. For instance, phenolated China fir bark PF resole was more viscous than phenolated Taiwan aca-

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Table 1
Elemental composition and chemical contents of white birch bark.

Elemental composition (wt%, d.b. ^a)				Chemical components (wt%, d.b. ^a)				
C	H	N	O ^b	Extractives ^c	Lignin ^d	Cellulose ^d	Hemi-cellulose ^d	Ash ^e
53.47	6.86	0.10	36.89	11.18	34.02	37.98	28.00	2.68

^a On a dry basis.

^b Determined by the difference between 100% and total carbon/hydrogen/nitrogen/ash content.

^c Determined by 70 vol% aqueous acetone extraction under stirring at room temperature for 3 h.

^d Determined in accordance with NREL/TP-510-42618, based on extractive and ash-free dry bark.

^e Determined by bark combustion at 575 °C.

cia bark PF resole, while phenolated Taiwan acacia bark PF resole showed a higher exothermic peak temperature and larger quantity of exothermic heat for curing than phenolated China fir bark PF resole. Using H₂SO₄ as the phenolation catalyst led to a higher viscosity of the liquid product while HCl contributed to a higher curing peak temperature for the resulted PF resole (Lee and Liu, 2003). Studies also revealed that additions of NaOH in multiple steps during phenolated bark PF resole synthesis contributed to a faster curing process, a lower free formaldehyde content, an acceptable curing rate for the resulted BPF and even better wet shear strength for the bonded 3-ply plywood (Gao et al., 2007; Yuan et al., 2009). However, the main limitation of using phenolated bark for PF resole synthesis is the low phenol substitution ratio, normally less than 30 wt%.

Using bark derived pyrolysis oil as a phenol alternative for PF resins preparation has been extensively reported. To date, there are a number of patents on the recovery of phenolic compounds from pyrolysis oil, as well as the application of pyrolysis oil for PF resoles (Chum et al., 1990, 1992, 1993; Roy et al., 2000). Amen-Chen et al. (2002a,b,c) pyrolyzed softwood bark at 505 °C under 18 kPa, then applied the pyrolysis oil in partially substituting phenol for BPF resole synthesis. It was found that BPF resole with 25 wt% phenol substitution by softwood bark pyrolysis oil cured in very similar kinetics to a lab synthesized neat PF resole. However, when phenol substitution exceeded 50 wt%, the resulted BPF resoles showed a lower condensation extent. Furthermore, increasing phenol substitution reduced the thermal resistance of the resulted BPF resoles. When using the bark pyrolysis oil-based BPF resoles as wood adhesives, OSB bonded with the BPF resole at phenol substitution of 25 wt% or 35 wt% showed satisfactory MOR, MOE and IB, physical thickness swelling, exceeding the minimum requirements of CSA 0437–1993 Standard in both dry and wet tests (after 2 h boiling in water) (Chan et al., 2002).

Hydrothermal liquefaction (HTL) of lignocellulosic biomass for phenolic bio-crude is a promising pathway to increase phenol substitution ratio in BPF resoles synthesis. Cheng et al. (2011) produced bio-crude through HTL of eastern white pine (*Pinus Strobus* L.) sawdust in hot compressed water/ethanol (50:50, v/v) mixture, then used the obtained bio-crude to replace up to 75 wt% phenol in BPF resole synthesis. The obtained 75 wt% BPF resole displayed chemical and curing properties as well as dry/wet bonding strengths for plywood, comparable to a neat PF resole.

In our previous studies (Feng et al., 2014), bark liquefaction in hot compressed water/ethanol (50:50, v/v) mixture contributed to very high yields of bio-crude oils. It was also revealed that the bark-derived bio-crude contains a high content of phenolic compounds derived from tannin and lignin, which makes it a suitable substitute for phenol in BPF resoles synthesis. As well known, bark contains a lot of extractives (consisting of phenolic compounds such as tannin), which may affect the BPF resoles when bark-derived bio-crude is used as a phenol substitute. However, effects of extractives on the properties of BPF resoles have not been explored by far. Meanwhile, bark-derived bio-crude oil contains water-soluble fraction that originates from the degradation of cellulose and hemicellulose. The water-soluble fraction in the bark-derived bio-crude oil

could also affect the properties of the resulted BPF resoles, which is yet to be clarified. The present study aims at clarifying the effects of bark extractives and water-soluble fraction of bark-derived HTL-oil on the properties of the resulted BPF resoles.

2. Materials and methods

2.1. Materials

White birch bark was kindly provided by a local wood mill in Thunder Bay, Ontario, Canada. The bark was air-dried and ground into particles of 20 mesh. Elemental composition and chemical contents of the bark are as presented in Table 1. Anhydrous ethyl alcohol (ethanol) and acetone (≥99.5%) were purchased from Caledon Laboratory Chemicals, Canada. ACS reagent grade formaldehyde (37% aqueous solution) and sodium hydroxide solution (50% aqueous solution) were purchased from EMD, Germany. Phenol (≥99.0%) was provided by Sigma–Aldrich.

2.2. Methods

2.2.1. Preparation of HTL-oil, eHTL-oil, and fHTL-oil

White birch bark was liquefied in water/ethanol (50:50, v/v) mixture to produce liquid product (HTL-oil in short) in a 500 mL Parr reactor. In a typical run, 25 g white birch bark and 250 mL water/ethanol (50:50, v/v) mixture were charged into the reactor and stirred at 175 rpm. Residual air in the reactor was removed by alternate vacuuming–N₂ purge for three times. The reactor was then pressurized with 2.0 MPa N₂ and heated at 10 °C/min to 300 °C. After 15 min liquefaction at 300 °C, the reactor was cooled down to room temperature in a water/ice bath. Gas in the reactor was vented. The reactor was opened and rinsed with acetone. The slurry and rinsing acetone were collected and filtered. Acetone, ethanol and water in the filtration liquid was removed at 45 °C, 60 °C and 75 °C through rotary evaporation under reduced pressure. The obtained dark viscous product was vacuum-dried at 60 °C for 24 h and designated as HTL-oil with a yield of 66.5 wt%.

fHTL-oil was obtained in the following procedures: white birch bark was first liquefied in water/ethanol (50:50, v/v) mixture as described in the previous paragraph for HTL-oil production. After the liquefaction and filtration, acetone and ethanol were recovered by rotary evaporation at 45 °C and 60 °C under reduced pressure, respectively. After removal of acetone and ethanol, the vacuum was released and the rotary evaporator was kept on at 60 °C under atmospheric pressure for 15 min, then the aqueous fraction containing water-soluble fraction in the flask was decanted. 50 mL distilled water was added into the evaporation flask, followed by 15 min rotary evaporation at 60 °C under atmospheric pressure and the aqueous fraction was decanted again. The above water-washing process was repeated until the aqueous fraction became colorless. The water insoluble residue remained in the flask was then vacuum-dried at 60 °C for 24 h and designated as fHTL-oil with a yield of 41.5 wt% based on the bark.

As for the eHTL-oil production, air dried white birch bark was first extracted in 70 vol% aqueous acetone under stirring at the

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