EFFECTS OF HOT-WATER TREATMENT OF BLACK SPRUCE AND TREMBLING ASPEN BARK RAW MATERIAL ON THE PHYSICAL AND MECHANICAL PROPERTIES OF BARK PARTICLEBOARD

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(Received December 2007)

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Wood and Fiber Science, 40(3), 2008, pp. 339–351

Abstract. The understanding of the interaction between bark extractives and adhesives is fundamental in the manufacture of bark particleboard for optimum adhesive curing, and mechanical and physical properties of the boards. The effect of hot-water treatment on black spruce and trembling aspen bark was investigated to highlight its impact on the bark particles/phenol-formaldehyde adhesive system, and on the physical and mechanical properties of bark particleboard made from hot-water-treated bark of both species. Bark was soaked in hot water maintained at 100°C for 3 h. The results showed that the hot-water treatment affects the physical and chemical properties of the bark by decreasing hydrophilic characteristics, acidity, and the amount of condensable polyphenols that can react with formaldehyde. The mechanical properties, including static bending and internal bond of particleboard made from untreated black spruce and trembling aspen bark, were higher than those of boards made from hot-water-treated bark of the same species. The thickness swelling of particleboard made from hot-water-treated black spruce and trembling aspen bark was higher than that made from untreated bark. One exception occurred for particleboard made from 100% trembling aspen bark for which no significant difference was found between particleboards made from treated and untreated barks.

Keywords: Bark, hot-water treatment, extractives, PF adhesive curing, particleboards, physical and mechanical properties.

INTRODUCTION

Large quantities of bark produced in the Province of Quebec, Canada, are mostly used for thermal energy production (Anon 2007). However, research efforts are underway to foster the use of bark for higher value-added products such as alternative raw materials for particleboard manufacturing (Blanchet 1999; Blanchet et al 2000; Villeneuve 2004; Ngueho Yemele et al 2007a, 2007b). The use of bark in wood particleboard manufacturing is currently viewed negatively due to significant adverse effects on strength and dimensional properties resulting from excessive bark content in the raw material. Previous work demonstrates a decrease in static bending including modulus of elasticity (MOE), modulus of rupture (MOR), and internal bond (IB) with increasing bark content, while linear expansion (LE) increased (Dost 1971; Lehmann and Geimer 1974; Wisherd and Wilson 1979; Muszynski and McNatt 1984; Blanchet et al 2000; Ngueho Yemele et al 2007a, 2007b).

Bark is a source of numerous extractives used for several applications including pharmacology and adhesive production. However, extractives in the raw material can have adverse effects on the setting of adhesives, lowering the particle-particle bond strength, increasing the risks of blows, and severely reducing IB strength (Moslemi 1974). On the other hand, phenolic extractives can react with formaldehyde and limit water uptake as well as improve thickness swelling resistance of the board (Moslemi 1974; Anderson et al 1974a, 1974b, 1974c; Plackett and Troughton 1997; Nemli et al 2004a, 2004b, 2006; Nemli and Colakoglu 2005). For instance, a significant improvement was found for thickness swelling, decay resistance, and formaldehyde emissions of particleboard made from bark particles as well as wood particles impregnated or sprayed with bark extractives (Anderson et al 1974a, 1974b, 1974c; Nemli et al 2004a, 2004b, 2006; Nemli and Colakoglu 2005). However, the mechanical properties of those boards were lower than for panels made from unimpregnated wood particles (Nemli et al 2004a, 2004b). Therefore, a better understanding of the impact of bark extractives on adhesion is fundamental to improve adhesive curing as well as bark particleboard strength and dimensional stability.

Phenol-formaldehyde (PF) adhesive is one of the most widely used wood adhesives. Its curing speed depends strongly on wood pH, explaining why high alkalinity accelerates polymerization (Moslemi 1974). He and Riedl (2004) reported that PF curing is influenced by the interactions between the adhesive and the raw material. Significant work has been done on the effect of wood on the curing reactions of PF adhesive (Chow 1969; Chow and Mukai 1972; Mizumachi and Morita 1975; Pizzi et al 1994; Lee et al 2001; He and Riedl 2004; He and Yan 2005).

However, some results are somewhat contradictory. In the presence of wood, the activation energy of curing reactions of adhesives is lowered (Chow 1969; Pizzi et al 1994; He and Yan 2005). When a PF resin cures on a wood surface, the polymeric constituents of the substrates induce two effects which lower the activation energy (Pizzi et al 1994). The first and major cause of the reduction is the catalytic activation of resin self-condensation induced particularly by carbohydrates such as crystalline and amorphous cellulose, and hemicelluloses. The second and minor cause is the formation of resin/substrate covalent bonding, particularly for lignin. On the other hand, some results (Mizumachi and Morita 1975; He and Riedl 2004) indicate that the curing reaction of phenolic adhesive could be delayed by some wood species, resulting in higher activation energy of PF adhesive. He and Riedl (2004) ascribed the aforementioned contradiction to the impact of wood on the curing reactions of PF adhesive to the complex effect due to different wood structure and chemical composition (pH), as well as different experimental methods and conditions.

Cold-water wood extractives from various species had little or no effect on the hardening characteristics and the curing of urea-formaldehyde (UF) adhesive (Stefke and Dunky 2006). The addition of merbau (*Intsia sp.*) wood extractives caused a reduction of pH and slightly increased the gelation rate of PF resin (Tohmura 1998). Buffering capacity and pH are important factors impacting PF adhesive curing (He and Riedl 2004). A decrease of the PF/particle system pH led to a decrease of the adhesive functional group reactivity.

Lee et al (2001) reported that PF resin gel time was not correlated to flake pH and buffer capacity of the wood species. In contrast, a better correlation was observed between total acids and gel time than between soluble acids and gel time (Subramanian et al 1983).

The objectives of this study were 1) to investigate the effect of hot-water treatment on black spruce and trembling aspen bark, and 2) to highlight the effect of hot-water treatment on the bark particle/PF adhesive system, and its consequences on the physical and mechanical properties of particleboard made from hot-water-treated bark.

MATERIAL AND METHODS

Bark Particle Production

Fresh black spruce (*Picea mariana* (Mill.)) and trembling aspen (*Populus tremuloides* (Michx.)) bark samples were collected from Arbec Forest Products Inc. softwood sawmill located in L'Ascension, Québec and the Louisiana Pacific Canada OSB mill located in Chambord, Québec, respectively. The raw bark samples were taken directly from the debarking units in each mill. One-half of the bark collected was stored in a cold chamber at −5°C for extractions. A laboratory dry kiln at 60°C was used to dry the other part to a final moisture content of 5%. Bark density, wood content of the bark residues, and effective bark content of the panels were also determined (Ngueho Yemele et al 2007a).

Hot-Water Treatment

Because of its low cost and environmental impact, water was chosen to produce extracted particles for particleboard manufacturing. Bark was soaked in warm water at an initial temperature of 55°C. The mean concentrations were 35 and 28 g oven-dried weight of bark particles per liter of water for black spruce and trembling aspen, respectively. The system was heated with water vapor and the average temperature maintained at 100°C for 3 h. The weight loss, including the extracted compounds and undesirable materials such as sand and stone, was determined gravimetrically. The weight loss reported as a percentage of the dry raw material was 16.6 and 10.8% for black spruce and trembling aspen, respectively.

Crushing of Raw Bark and Sieving of Bark Particles

Both kiln-dried untreated and air-dried treated bark were crushed in a hammer mill and sieved

in four groups: one for the surface layer and three others, fine, medium and coarse, for the core layer. Wood and bark particles were mixed to produce the particleboards. The particle size distribution of both untreated and treated bark as well as wood was determined with a CE Tyler testing sieve shaker. Results obtained for surface and core layer particles have been reported (Ngueho Yemele et al 2007a, 2007b). In addition, bark and wood particles were oven-dried under vacuum at 70°C for 24 h, and then cooled for about 30 min under P_2O_5 before chemical analysis and gel time measurement.

Physical and Chemical Analyses of Bark Particles

The bark specimens were sampled and prepared according to the Tappi standard method T257 (Tappi 2002). The insoluble lignin content was determined by the modified Klason method Tappi T222 (Tappi 2006) according to the procedure described by Lawoko et al (2006), and the acid-soluble lignin was quantified using absorption spectroscopy at 205 nm using Tappi useful method UM-250 (Tappi 1991). The holocellulose content of extractive-free samples was determined by the chlorite method (Wise et al 1946) and was corrected for residual lignin after hydrolysis of the holocellulose with sulphuric acid. The cellulose content was determined by the Kurschner and Hoffer nitric acid method (Browning 1967).

Total extractive contents of both untreated and treated bark were determined by successive extractions of bark flour with organic solvents (first with hexane and then denatured ethanol) and hot water according to Tappi standard methods T 204 and T 207 (Tappi 2007b, 1999). Ash contents were determined according to Tappi standard method T 211 (Tappi 2007a).

Total acid-value of particles was estimated according to the procedure described by Subramanian et al (1983). This method allows the quantification of both insoluble and water-soluble acids present in the particles. The reaction of the particles with 0.1-M sodium acetate releases an equivalent amount of acetic acid which is related to total acidity. A 10-g specimen of dry bark flour was placed in a 250-mL Erlenmeyer flask with 100 mL of 0.1-M sodium acetate solution under continuous stirring (250 rpm) at room temperature for 24 h. Afterward, the mixture was filtered through a Whatman No 4 filter paper in a Büchner funnel by vacuum; 20 mL pipetted from the filtrate was diluted to 40 mL before titration. After recording the initial pH, 40 mL of extract solution was titrated potentiometrically with 0.025-N NaOH solution to reach the equivalence point. The total acid value (TAV) was obtained by the following equation:

$$\mathrm{TAV(meq.mol/100\ g\ of\ bark)} = \frac{V \times [\mathrm{NaOH}]}{W} \times 100 \quad (1)$$

where V is the volume (mL) of the NaOH titration solution used for a given bark sample to reach the equivalence point, [*NaOH*] the normality of NaOH, and W the weight of raw bark or wood (g) used for titration.

The hydrophobic/hydrophilic behavior of bark particles was determined from the contact angle (θ) measurements with water, using a KRÜSS 2570 Processor Tensiometer (KRÜSS, Germany) at 20°C. This method is based on measuring the change in sample mass during adsorption of liquids (Persin et al 2002). Specimens of oven-dry mass of 0.25 g for each bark type and 0.15 g for wood particles were used. The contact angle between bark particles and water was calculated using the Washburn equation (Washburn 1921), a measurement method used to determine the sorption behavior of solids:

$$\cos\theta = \frac{m^2 \times \eta}{t \times \rho^2 \times \gamma \times c} \quad (2)$$

where θ = contact angle between solid and liquid phases (°), m = sample mass (kg), η = liquid viscosity (mPa · s), t = time (s), ρ = liquid density (kg · m^{-3}), γ = surface tension of the liquid (mN · m^{-1}), c = material constant of capillarity (m^5). Hexane was used as a complete wetting liquid to determine the constant of cap-

illarity of each raw material (untreated and treated bark particles).

Interaction Between Bark Particles and PF Resin

Stiasny numbers, which reflect formaldehyde-condensable polyphenol content, were determined following the procedure proposed by Yazaki and Hillis (1980). For each raw material, the aqueous extract was prepared by refluxing 25 g of dry bark flour in 250 mL of distilled water for 1 h. The mixture was then filtered through a Whatman no 4 filter paper in a Büchner funnel under vacuum. The solid residues were washed twice with an additional 125 mL of hot distilled water. The combined filtrates were then cooled to room temperature and freeze-dried. A sample of 100 mg of aqueous extract was dissolved in 10 mL distilled water. One mL of 10-N HCl and 2 mL of formaldehyde (37%) were added and the mixture was heated under reflux for 30 min. The reaction mixture was filtered while hot through a sintered glass filter. The precipitate was washed with hot water (5 × 10 mL) and dried over P_2O_5. The yield of formaldehyde-condensable polyphenols was expressed as a percentage of the weight of the starting material. The percentage formaldehyde-condensable polyphenol content in each raw bark material was calculated by multiplying the extractives yields by the Stiasny value and dividing by 100.

A liquid PF adhesive from Dynea Company Ltd was used. The solid content of the adhesive was 55% and the pH was 10.7. Gel time measurements were made with a Sunshine Gel Time Meter (Fisher, USA). The effects of both untreated and treated bark powder on the gel time of PF adhesive were investigated by mixing 0.4 g of dry powdered raw bark and 5 g of liquid PF adhesive in a 15 × 150 mm test tube heated in a 120°C glycerin solution.

Bark Particleboard Manufacturing

Particleboards measuring 560 × 460 × 8 mm with a target density of 800 kg/m^3 were manufactured using a 1000 × 1000 mm Dieffenbacher hot press equipped with a PressMAN control system (Alberta Research Council). A liquid PF adhesive from Dynea Company Ltd was used. The adhesive content was determined by a procedure described in Ngueho Yemele et al (2007a) to maintain a constant adhesive content per unit particle specific surface (kg m^{-2}). Therefore, adhesive contents of 9, 5, and 3% were used in core layer for particleboards made from 100% bark content of untreated and treated fine, medium, and coarse particle size, respectively. Likewise, 9, 7, and 6% of adhesive were used for particleboard made from 50% untreated and treated bark content of fine, medium, and coarse particle size, respectively. Panels were pressed at a platen temperature of 200 ± 0.1°C with 20-s press closing, 200-s curing, and 60-s opening times that resulted in a total press cycle of 280 s. Wax additions of 1 and 0.5% were made to the surface and core layer particles, respectively, in the blender.

The manufactured panels were conditioned at 20 ± 3°C and 65 ± 1% RH for 1 wk. The physical and mechanical properties were determined according to the ANSI standard A.208.1–1999 (ANSI 1999). The properties determined were MOE and MOR in static bending, IB, and TS. These properties were chosen because of the relationship between each of them and the extractives/PF adhesive system. However, to consider the impact of sample density on the physical and mechanical properties of particleboards, other dependent variables such as the specific MOE (MOE_{spec} = MOE/sample density), the specific MOR (MOR_{spec} = MOR/sample density), the specific IB (IB_{spec} = IB/sample density), and the specific TS (TS_{spec} = TS/sample density) were used to perform statistical analyses.

Experimental Design and Data Analyses

The factorial design was used in this work. The factors studied for each species were bark state (untreated and treated), bark content (50 and 100%), and bark particle size of the core layer (fine, medium, coarse). For mixed bark and

wood particleboards, a bark content of 50% was used in both surface and core layers. The blending of bark (untreated or treated) and wood particles was made in a rotary blender to obtain a homogeneous mixed furnish material. This led to 12 combinations with 3 replicates resulting in a total of 36 panels for each bark species. For all chemical analyses, two replicate measurements for each sample were made.

The Statistical Analysis System (SAS) software 9.1 was used for statistical analyses. The analysis of variance (ANOVA) and contrasts between the factors were performed at 12 levels. When an interaction between bark state and one or both of the two other factors was significant, the values of those factors were fixed in the SAS model with the procedure called "slice" to assess the effect of hot-water treatment (bark state) on the properties of particleboard made from black spruce and trembling aspen bark. Interaction curves of factors were provided.

RESULTS AND DISCUSSION

Characteristics of Black Spruce and Trembling Aspen Bark

The chemical composition of black spruce and trembling aspen bark is presented in Table 1. The holocellulose content of treated black spruce and trembling aspen bark was higher than reported by Harun and Labosky (1985) for some northeastern American softwood and hardwood barks that ranged about 36–44% and 36–47%, respectively. The lignin content of black spruce and trembling aspen bark was found to be 31.9 and 30.7%, respectively, significantly lower than that of most American softwood and hardwood bark (Harun and Labosky 1985). Nevertheless, the lignin content of black spruce bark was similar to the 31.6% obtained by Geng et al (2006). The hot-water solubility of black spruce bark was much lower than the 26.8% found by Geng et al (2006). The bark residues used in this work were collected from the debarking units at sawmills and OSB plants. Wood contents of 18.1 and 11.9% were found for black spruce and trembling aspen bark residues, respectively. It is well known that wood contains less lignin and extractives, and more cellulose than bark. The ash content of untreated black spruce bark residues was 19.6% (Table 1), which is much greater than the 2.6% obtained by Geng et al (2006). Although ash content for hardwood and softwood bark ranged from about 1–10% (Harun and Labosky 1985), raw bark residues collected from debarking units often contain sub-

TABLE 1. *Bark organic and inorganic extractive content, total acidity and contact angle.*

	Main groups	Black spruce bark		Trembling aspen bark	
		Untreated	Treated	Untreated	Treated
		(%)			
	Holocellulose*	54.8	—	66.2	—
	Cellulose*	34.1	—	34.5	—
	Total lignin*	31.9	—	30.7	—
Successive extractions					
Hexane	Fatty acids, fats, oils, waxes, resins, resins acids, sterols.	3.7	3.5	6.5	6.6
Denatured ethanol	Coloring matter, stibenes, polyphenols.	8.2	4.0	6.5	2.4
Hot water	Carbohydrates, proteins, alkaloids, ash, tannins.	9.5	8.1	13.3	6.1
Total		21.4	15.6	26.3	15.1
Direct hot-water extraction		12.7	11.5	17.7	10.2
Ash	Inorganic extractives.	19.6	13.9	5.1	5.4
	Silica	7.5	5.3	—	—
Total acidity		1.76	1.70	2.06	1.63
Contact angle (°)		79	88	63	87

*: calculation based on extractive-free bark

stantial amounts of undesirable materials such as sand. In the case of the black spruce bark used in this work, the presence of sand in the raw material significantly increased the silica content as well as the entire ash content of the bark residues. The ash content of untreated trembling aspen bark was 5.1% (Table 1), similar to that reported by Fournier and Goulet (1971).

Chemical Impacts of Hot-Water Treatment

Comparison between extractive contents of treated and untreated bark (Table 1) shows differences in both denatured ethanol and hot-water solubility values. However, there was no effect of the hot-water treatment applied to the lipophilic extractives exhibited by hexane solubility. Likewise, the polyphenol condensable content of treated bark was much lower than that of the untreated bark (Table 1). This implies that the extractives removed by the hot-water extraction do not belong to the lipophilic substances group.

Knowledge of the raw material acidity (unextracted and extracted bark, wood) is important for understanding the adhesive curing process. The Subramanian et al (1983) method was chosen because they observed a better correlation between total acids and gel time than between soluble acids and gel time. The reaction of insoluble or bound wood/bark carboxylic acids (WB-COOH) with sodium acetate can be simplified as follows:

$$\mathrm{WB{-}COOH} + \mathrm{CH_3COONa} \rightleftarrows \mathrm{WB{-}COONa} + \mathrm{CH_3COOH} \quad (3)$$

The total acidity values (TAV) of treated bark are lower than that of untreated bark as shown in Table 1. The hot-water treatment extracts soluble acidic compounds from the bark and decreases its TAV. We can also observe that all bark particles (treated and untreated) are more acidic than wood due to their high extractive contents.

Figure 1 presents the water uptake velocity of bark (untreated and treated) and wood particles. The values of contact angle are presented in

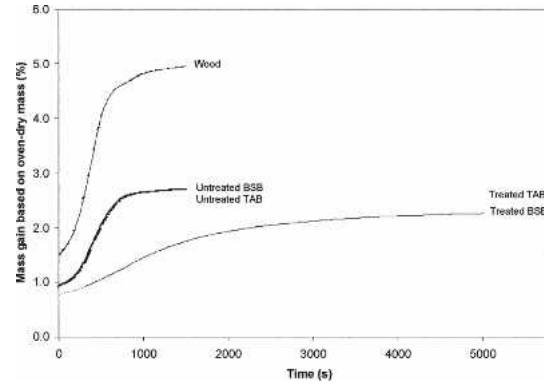

FIGURE 1. Mass gain based on oven-dry mass of wood particles, untreated and treated bark particles during water absorption (BSB = Black spruce bark; TAB = trembling aspen bark).

Table 1. Comparison of the two barks showed that the hot-water treatment increased their hydrophobicity, indicated by high contact angle values. This confirms that hot-water treatment removes –OH group compounds such as polyphenols and free carbohydrates. These –OH groups are responsible for better adsorption characteristics. A larger number of available –OH groups means a higher probability of interaction between the material and water. However, the hot-water treatment decreases the adsorption ability of the bark. Untreated bark adsorbs the largest amount of water. As a result, its weight increases more than treated bark after water uptake, as illustrated in Fig 1. Overall, wood absorbs the highest amount of water. The reason for these differences is based on the structural and morphological characteristics of bark particles.

Effect of Hot-Water Treatment on Gel Time

Results of the effect of hot-water treatment on adhesive gel time are reported in Table 2. Hot-water treatment had a negative effect on the quality of the condensable polyphenols that can react with formaldehyde. This resulted in a decrease of the Stiasny number calculated from similar quantities of extracts. The most efficient condensable polyphenols were most likely removed during the treatment process or they were degraded by the hot-water treatment (oxidation

TABLE 2. *Stiasny number and gel time of raw material.*

Raw material	Stiasny number	Formaldehyde-condensable polyphenol content (%)	Gel time (s)
Untreated BSB	30.62	3.9	854
Treated BSB	20.50	2.4	837
Untreated TAB	7.53	1.3	891
Treated TAB	1.17	0.2	869
Wood	—	—	822

BSB = black spruce bark particles; TAB = trembling aspen bark particles.

of phenolic groups –OH to quinonic –C=O) resulting in a decrease of condensable polyphenol content of the bark extract. The gel time of bark particles decreased after the hot-water treatment. The hot-water treatment lowers the total acidity of the bark particles and improves PF resin curing. The curing of the PF adhesive is negatively affected by the raw material acidity which is in agreement with the findings of He and Riedl (2004). They reported that acidity is an important factor influencing the PF resin curing. A decrease of the pH of the PF/particle system led to a decrease of the resin functional groups reactivity.

Effect of Hot-Water Treatment of Bark on the Mechanical and Physical Properties of Bark Particleboard

ANOVA results of the contrasts between bark state (treated and untreated) and the other factors (bark content and bark particle size) on the mechanical and physical properties of bark particleboard are summarized in Tables 3 and 4. The effect of bark content and bark particle size on the physical and mechanical properties of particleboard made from black spruce and trembling aspen bark was discussed in previous reports (Ngueho Yemele et al 2007a, 2007b). Detailed analyses of the effect of hot-water treatment of bark on mechanical and physical properties of the particleboards are presented in the following sections.

Bending strength. Tables 3 and 4 show a significant effect of bark state on the specific static bending properties (MOE_{spec} and MOR_{spec}) of

TABLE 3. *Results of the analysis of variance of the contrasts with bark state (F values) for physical and mechanical properties of particleboard made from black spruce.*

Source of variation	Physical and mechanical properties			
	MOE_{spec}	MOR_{spec}	IB_{spec}	TS_{spec}
Bark state	296.58**	194.03**	90.01**	139.15**
[1] Bark state x bark content (BC)	36.42**	16.62**	10.85**	0.19^{NS}
[2] Bark state x bark particle size (BPS)	3.21^{NS}	0.40^{NS}	1.13^{NS}	8.41**
[3] Bark state x BC x BPS	3.36^{NS}	2.50^{NS}	4.57*	3.10^{NS}
(1) sliced by bark content				
50	270.43**	162.11**	—	—
100	62.57**	48.54**		
(2) sliced by bark particle size				
Fine				27.88**
Medium	—	—	—	24.94**
Coarse				103.12**
(3) sliced by BC x BPS				
50% Fine			6.18*	
50% Medium			12.69**	
50% Coarse	—	—	2.36^{NS}	—
100% Fine			13.97**	
100% Medium			17.79**	
100% Coarse			59.26**	

MOE = modulus of elasticity, MOR = modulus of rupture, IB = internal bond, TS = thickness swelling,
MOE_{spec} = MOE divided by sample density, MOR_{spec} = MOR divided by sample density, IB_{spec} = IB divided by sample density, TS_{spec} = TS divided by sample density. NS: not significant at 0.05 probability level. *: significant at 0.05 probability level. **: significant at 0.01 probability level.

TABLE 4. *Results of the analysis of variance of the contrasts with bark state (F values) for physical and mechanical properties of particleboard made from trembling aspen.*

Source of variation	Physical and mechanical properties			
	MOE_{spec}	MOR_{spec}	IB_{spec}	TS_{spec}
Bark state	98.98**	51.83**	15.45**	67.42**
[1] Bark state x bark content (BC)	13.91**	22.35**	0.93^{NS}	55.86**
Bark state x bark particle size (BPS)	1.96^{NS}	0.06^{NS}	1.02^{NS}	1.13^{NS}
Bark state x BC x BPS	2.42^{NS}	1.72^{NS}	1.91^{NS}	2.28^{NS}
(1) sliced by bark content				
50	19.34**	3.06^{NS}	—	123.01**
100	93.54**	71.12**		0.27^{NS}

MOE = modulus of elasticity, MOR = modulus of rupture, IB = internal bond, TS = thickness swelling,

MOE_{spec} = MOE divided by sample density, MOR_{spec} = MOR divided by sample density, IB_{spec} = IB divided by sample density, TS_{spec} = TS divided by sample density. NS: not significant at 0.05 probability level. *: significant at 0.05 probability level. **: significant at 0.01 probability level.

particleboard made from black spruce and trembling aspen at the 0.01 probability level. In addition, there is also a significant effect of the interaction between bark state and bark content on the MOE_{spec} and MOR_{spec} at the 0.01 probability level. This suggests that the effect of bark state depends on bark content. The decomposition of the interaction between bark state and bark content with the SAS procedure named "slice" exhibits a significant effect of the bark state on each level of bark content (50 and 100%) of both species except for the 50% trembling aspen bark as shown in Tables 3 and 4. Figures 2 and 3 obviously show that the static bending properties (MOE and MOR) of the particleboard made from untreated bark of both species are higher than those of that made from treated bark except for boards of 50% trembling aspen bark content with no significant difference on the MOR between untreated and treated bark (Fig 3). Thus, the MOE and MOR of the boards made of 50 and 100% black spruce bark content decreased by 25 and 22%, respectively, due to the bark state (treated vs untreated) (Figs 2 and 3). Likewise, the MOE and MOR of the boards made of 100% trembling aspen bark content decreased by 34 and 38%, respectively. In contrast, slight (9%) and no significant effects were respectively noticed on the MOE and MOR of particleboard made from 50% trembling aspen bark (Figs 2 and 3). The decrease in bending strength due to the bark state was similar to 50 and 100% black spruce bark content. On the other hand, there was a significant difference for

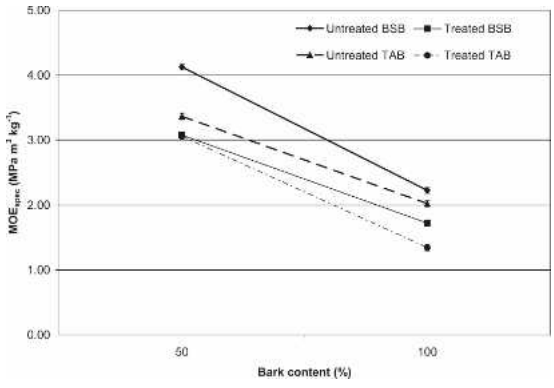

FIGURE 2. Effect of hot-water treatment of black spruce (BSB) and trembling aspen (TAB) bark on the specific modulus of elasticity (MOE_{spec}) of particleboard made from black spruce and trembling aspen bark.

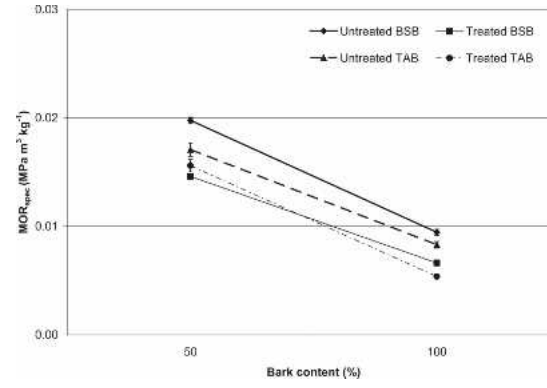

FIGURE 3. Effect of hot-water treatment of black spruce (BSB) and trembling aspen (TAB) bark on the specific modulus of rupture (MOR_{spec}) of particleboard made from black spruce and trembling aspen bark.

the trembling aspen bark content between 50 and 100%.

Internal bond. Tables 3 and 4 show a significant effect of bark state on IB_{spec} of particleboard made from black spruce and trembling aspen bark at the 0.01 probability level. Table 3 also indicates a significant effect of the triple interaction among bark state, bark content, and bark particle size on the IB_{spec} of the particleboard made from back spruce bark at the 0.05 probability level. This means that the effect of bark state on the IB depends on the two other factors. The decomposition of the source of variation of that interaction presented in Table 3 shows a significant difference between the IB_{spec} of boards made from untreated and treated bark for all the combinations of bark content and bark particle size except for 50% of coarse bark particles. Figure 4 shows that IB strength of particleboard made from untreated black spruce is higher than that of the boards made from treated bark except for 50% bark content of coarse particles. In fact, due to the low bark content in coarse particles, bark state did not significantly affect the IB of those boards. Thus, IB_{spec} of the boards made from black spruce bark content decreased by 30 to 67% due to the bark state except for those made from 50% of coarse particles. IB_{spec} values of particleboard made from treated and untreated trembling aspen were 0.47 and 0.56 kPa · m^3/ kg, respectively. This shows

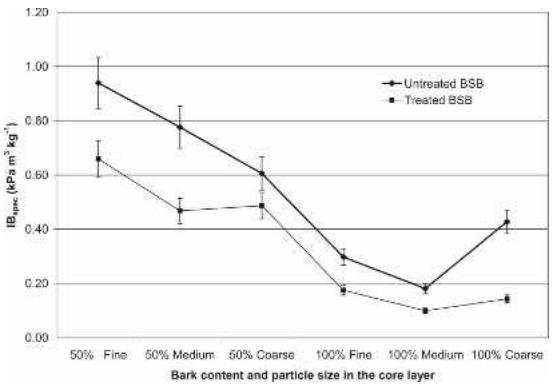

FIGURE 4. Effect of hot-water treatment of black spruce bark (BSB) on the specific internal bond (IB_{spec}) of particleboard made from black spruce bark.

that a decrease of 16% on the IB_{spec} of all the particleboard made from trembling aspen bark and can be attributed to bark state.

The mechanical properties of particleboard made from black spruce bark and trembling aspen were found to be lower than that of the control (100% wood particles) (Ngueho Yemele et al 2007a). This could be due to the fact that the bark particles increased the acidity of PF adhesive, which could have extended the gel time of PF adhesive and inhibited its curing. In addition, the weaker mechanical strength of bark could also contribute to the lower mechanical properties of particleboard with bark. The results of gel time shown in Table 2 indicated that the bond between PF adhesive and wood particles could be stronger than the bond between PF adhesive and bark particles, because the higher pH is more favorable to improve the bond quality of PF adhesive. In contrast, and in spite of the low acidity of treated bark, the mechanical properties of particleboard made from treated (extracted) bark were often lower than those of untreated ones. The reason may be the decrease of the effective lowering of molar ratio due to the drop of reactive material, like condensable polyphenols with formaldehyde. However, it is more likely that the hydrophobicity of the treated bark particles was responsible for the decrease of the mechanical properties. We observed that hot-water treatment did not remove the lipophilic extractives (Table 1). Therefore, the share of lipophilic extractives of extracted particles increased in comparison with the other extractive groups. It seems that they had more difficulty in being covered by the adhesive during gluing. The decrease of mechanical properties of the particleboard made from extracted bark would be mainly due to the weakness of the adhesive bonds in the bark particle matrix.

Thickness swelling. Tables 3 and 4 show a significant effect of bark state on the TS_{spec} of particleboard made from both species at the 0.01 probability level. In addition, there was a significant effect of the interaction between bark state and bark particle size, and between bark state

and bark content on the TS_{spec} of the boards made from black spruce and trembling aspen bark, respectively, at the 0.01 probability level. Thus, the effect of bark state depends on bark particle size and bark content of black spruce and trembling aspen, respectively. Sliced contrasts presented in Table 3 show a significant difference between the TS_{spec} of the particleboard made from untreated and treated bark of three different size classes (fine, medium, coarse). Likewise, Table 4 indicates a significant difference on the TS_{spec} of the particleboard made of 50% trembling aspen bark content. As shown in Fig 5, an increase of 42, 28, and 100% was observed on the TS of the boards of fine, medium, and coarse particles of black spruce bark, respectively, due to the hot-water extraction applied. A large increase of 67% of TS attributed to bark extractives was noticed on the particleboard made from 50% trembling aspen bark content. On the other hand, particleboard made from 100% bark content of the same species was found not significantly different (Fig 6).

It was noticed that hot-water-treated bark particles were more hydrophobic than the untreated. This could result in a lower diffusion of the adhesive in the particles matrix. Also, the hot-water treatment has released the extractives from bark cells and increased their porosity. The swelling observed in the particleboard made from hot-water-treated bark can be related to the following two combined effects: the decrease of the amount of PF adhesive absorbed by treated bark as well as the increase of bark particles porosity following hot-water treatment.

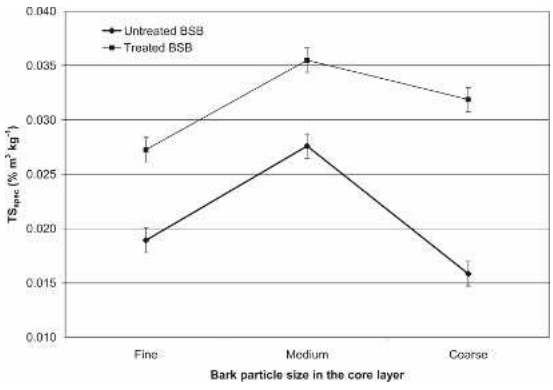

FIGURE 5. Effect of hot-water treatment of black spruce bark (BSB) on the specific thickness swelling (TS_{spec}) of particleboard made from black spruce bark.

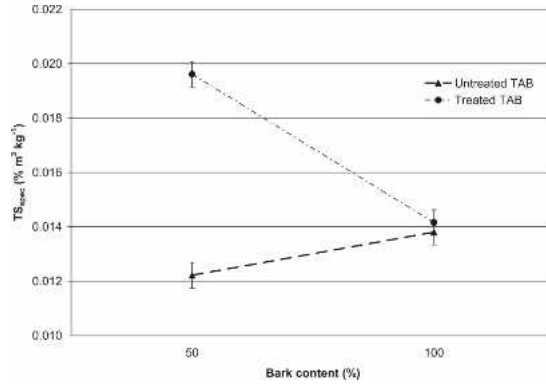

FIGURE 6. Effect of hot-water treatment of trembling aspen bark (TAB) on the specific thickness swelling (TS_{spec}) of particleboard made from trembling aspen bark.

CONCLUSIONS

The results obtained in this study lead to the following conclusions:

1. Hot-water treatment affects the physical and chemical properties of bark by decreasing the hydrophilic characteristic, the acidity, and the amount of condensable polyphenols that can react with formaldehyde. All these factors are of a great importance for the mechanical and physical properties of the particleboards.
2. Boards made from untreated black spruce and trembling aspen bark showed higher mechanical properties including modulus of elasticity, modulus of rupture, and internal bond than those made from treated bark of the same species.
3. The thickness swelling of boards made from treated black spruce and trembling aspen bark was higher than that of the boards made from untreated bark except for those made from 100% trembling aspen bark.

ACKNOWLEDGMENTS

The authors are grateful to the *Fonds québécois de la recherche sur la nature et les technologies*

(FQRNT), to the *Fonds de recherche forestière du Saguenay - Lac Saint Jean* and the *NSERC Research Discovery Grant no. CG082235* for funding this research. We also acknowledge the support of the *Arbec Forest Products* sawmill, L'Ascension, Québec, Canada, *Louisiana Pacific Canada* OSB plant, Chambord, Québec, Canada, and the *Tafisa* particleboard plant in Lac-Megantic, Québec, Canada for supplying bark residues and wood particles. We also thank the technicians of the *Centre de recherche sur le bois* for their support.

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