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Effects of hot water treatment of raw bark, coupling agent, and lubricants on properties of bark/HDPE composites

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ABSTRACT

Hot water treated and untreated black spruce bark (BSB) and trembling aspen bark (TAB) fibers were combined with high density polyethylene (HDPE) to produce bark thermoplastic composites by extrusion. Bark fibers of three size categories (fine, medium, and coarse) were used at contents of 50% and 60% based on oven dry weight. The effects of hot water treatment of raw bark and the addition of coupling agent (MAPE) and lubricants (OP-100, talc) on the flexural and tensile properties of bark/HDPE composites were investigated. Results showed a significant impact of hot water treatment on tensile properties of composites made with BSB and on tensile and flexural strength of composites made with TAB. The addition of coupling agent and lubricants significantly improved the flexural and tensile strength properties of bark/HDPE composites but reduced toughness and strain.

1. Introduction

Wood has been largely used by the plastics industry as an inexpensive filler to increase the strength and elasticity of thermoplastic and to reduce raw material costs. However, research on high filler content and coupling agents to improve interactions between wood and thermoplastic components led to the development of wood–plastic composites (WPCs), which offered synergistic material properties (Wolcott and Englund, 1999). The commercial success of these emerging materials has been mainly attributed to improved wood moisture performance, recycled and waste material utilization, and efficient product and process design (Wolcott and Englund, 1999). Lignocellulosic materials are lighter, much less abrasive, and renewable compared to other inorganic fillers (e.g., glass, clays, minerals) and have improved thermal stability over products made with unfilled material (FPL, 1999).

Large quantities of bark produced in the Province of Quebec, Canada are used mainly for thermal energy production (MRNF, 2007). Research has aimed to foster the use of bark in higher value-added products. Recent works emphasize the use of black spruce and trembling aspen bark as alternative raw materials for particleboard and medium fiberboard manufacturing (Ngueho Yemele et al., 2008a,b; Xing et al., 2006; Blanchet et al., 2000). However, only few reports examined the potential of bark as a fiber reinforcement or a filler for thermoplastic composites. Yemele et al. (2010) evaluated the potential of black spruce and trembling aspen bark fibers as thermoplastic filler. (Bouafif et al., 2009a) used jack pine bark particles to manufacture wood plastic composites by injection molding. They compared jack pine bark composite to composites made with different wood particles, including black spruce, jack pine, and eastern white cedar sapwood and heartwood particles. Results indicated that bark composites showed low mechanical properties compared to wood particle composites (Bouafif et al., 2009a) due to several factors including the higher extractives in bark (Bouafif et al., 2008). Thus, removing bark extractives for use in medicinal or esthetic purposes prior to thermoplastic composite manufacturing might be beneficial for the products mechanical behavior. In parallel to this study, Diouf et al. (2008,2009) investigated the antioxidant and anti-inflammatory activities of aspen and black spruce bark extracts.

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Several natural and biorenewable fibers such as straw, jute, wheat, soybean, kenaf, and sisal are used in the fiber/plastic composites industry (George et al., 2001). For optimal results, the fiber–matrix bond interface must be optimized when using natural fibers as reinforcement for plastics. Because fibers and matrices are chemically different, strong adhesion at the interface is required for effective stress transfer (George et al., 2001). Physical and chemical treatment methods are used to improve fiber–matrix compatibilization and adhesion. Correa et al. (2007) found good correlation between coupling efficiency and yield properties of wood composites with homopolymer and copolymer matrices within a range of varying wood-flour content and type of coupling agent.

Nachtigall et al. (2007) investigated the suitability of using polypropylene (PP) modified with organosilane as coupling agent for polypropylene/wood-flour composites compared to maleic anhydride modified PP. Results indicated that both coupling agents improved composite properties. However, silane modified PP produced composites with greater tensile strength, lower water absorption, and more homogeneous morphology than composites coupled with maleic anhydride modified PP. The silane modified polymer also improved interfacial adhesion between fibers and polymer matrix better than maleated polypropylene coupled composites.

Although several methods have been considered to improve fiber/polymer adhesion and enhance the performance of wood polymer composites, competition from certain lubricants can restrict compatibilizer access to the wood surface, while simultaneously altering the crystallization kinetics of the bulk polymer (Wolcott et al., 2001).

Bouafif et al. (2008) investigated the reaction of a variety of wood and bark fibers to MAPE treatment. Unlike chemical kraft fibers, bark fibers did not respond to the esterification reaction with MAPE treatment. They suggested that lignin concentration variability on the wood fiber surface is the main inhibiting factor for esterification. The complex three-dimensional structure of bark, with only some available reactive hydroxyl groups, largely explains this inhibition effect. Compared to several wood fibers, bark ranked last in ability to form ester bonds with polyethylene maleic anhydride (MAPE) (Bouafif et al., 2008).

Bark is a source of numerous extractives that can impact composite properties. The effect of wood flour extractives on the mechanical properties of wood–polypropylene composites has been investigated in previous works (Saputra et al., 2004; Kim et al., 2009). Higher flexural properties (modulus of rupture and modulus of elasticity) of pine and Douglas-fir flour composites were noted upon removal of extractives with different solvents, including acetone/water, dioxane/water, and benzene/ethanol (Saputra et al., 2004). Recently, Kim et al. (2009) found that WPC made with extracted wood flour from black cherry, eastern red cedar, and osage orange species had lower mechanical properties than unextracted WPC, whereas those made with extracted pine flour showed higher mechanical properties compared to unextracted pine WPC.

Despite similar solid wood properties and identical composite densities, the flexural properties of Douglas-fir/thermoplastic composite were significantly lower than those of pine composite. Similarly, the properties of WPC made with jack pine bark particles were lower than those of WPC made with different wood particles (Bouafif et al., 2009a). The wood–plastic interaction was suggested to explain the significant influence of wood species on WPC structure and properties (Wolcott, 2003). Bouafif et al. (2009a,b) linked WPC mechanical properties to the surface chemistry and relative crystallinity of fibers.

The objectives of this study were (1) to investigate the effects of hot water treatment of black spruce and trembling aspen raw bark material and (2) to evaluate the impact of the addition of coupling agent and lubricants on the mechanical properties of bark/high density polyethylene (HDPE) composites.

2. Materials and methods

2.1. Bark origin and fiber preparation

Fresh black spruce (*Picea mariana* (Mill.)) and trembling aspen (*Populus tremuloides* (Michx.)) bark samples were collected directly from debarking unit of a softwood sawmill, and from an oriented strandboard mill in Quebec Province, Canada. Half the collected bark was stored in a cold chamber at −5 °C for hot water treatment. The other half was dried in a laboratory dry kiln at 60 °C to a final moisture content of 5%. Bark density and wood content of bark residues were determined. Totals of 19.9 and 13.7% of wood (based on oven-dry weight) were found in black spruce and trembling aspen bark, respectively. Anhydrous density of the different bark species was determined by a volumetric method.

2.2. Hot water treatment of raw bark and refining

Due to its low cost and low environmental impact, water was chosen to extract raw bark to produce extracted and hot water treated bark fibers. Bark was soaked in warm water at an initial temperature of 55 °C. Mean concentration for both black spruce and trembling aspen was 28 g of oven-dried weight of bark particles per liter of water. The system was heated with water vapor for 3 h at a constant average temperature of 100 °C. Treated bark was air-dried. Weight loss, including extracted compounds and undesirable materials such as sand and stone, was determined gravimetrically. Weight loss, reported as a percentage of dry raw materials, was 12.9 and 12.0% for black spruce and trembling aspen, respectively.

Kiln-dried untreated and air-dried hot water treated bark were refined in a Pallmann double stream mill and sieved into three size categories: fine (0.18–0.25 mm), medium (0.25–0.50 mm), and coarse (0.50–1.00 mm). Bark fiber size distribution was determined with a CE approved Test Sieve Shaker (W.S. Tyler) and a fiber quality analyzer (FQA).

2.3. Chemical characteristics of bark

Bark specimens were sampled and prepared according to the Tappi T 257 cm-02 standard (Tappi, 2002). The chemical composition of the bark and wood fibers used in this study was determined and the results presented in a previous report (Yemele et al., 2010). Total bark extractive contents were determined by successive extractions from powdered bark using organic solvents (hexane, denatured ethanol, and hot water) according to Tappi T 204 cm-07 (Tappi, 2007a) and T 207 cm-99 (Tappi, 1999) standards. Ash contents were determined according to Tappi standard method T 211 om-07 (Tappi, 2007b). Two replicates for each sample were examined.

2.4. Compounding and processing of bark thermoplastic composites

Untreated and hot water treated black spruce and trembling aspen bark fibers of different sizes were used. High density polyethylene (Petrothene® LB 0100-00) with melt flow index of 0.40 g/10 min (measured according to ASTM D 1238) and density of 950 kg/m^3 was supplied by Equistar Chemical Company, Houston, TX, USA. The coupling agent, polyethylene maleic anhydride copolymer (MAPE – AC 575 A), was supplied by Honeywell Specialty Materials, Morristown, New Jersey, USA. Lubricant used was ester stearate OP-100 (Honeywell OptiPak), zinc stearate (Zn-st) (Chemical Distributors Inc. – CDI), and ethylene bis stearamide

Table 1
Formulations for bark/HDPE composites.

Formulation	Effect of hot water treatment, fiber origin proportion and length											
Fiber origin	Treated and untreated black spruce bark (BSB)						Treated and untreated trembling aspen bark (TAB)					
Fiber proportion	50%			60%			50%			60%		
HDPE proportion	45.3%			35.3%			45.3%			35.3%		
Fiber morphology	Fine	Medium	Coarse	Fine	Medium	Coarse	Fine	Medium	Coarse	Fine	Medium	Coarse
OP-100 lubricant	2.7%						2.7%					
MAPE (%)	2.0%						2.0%					

Fiber origin	Effect of lubricant and coupling agent Untreated trembling aspen bark (TAB)				Effect of talc Untreated trembling aspen bark (TAB)	
Fiber proportion	60%				58%	
HDPE proportion	39%	37%	38%	36%	39%	32%
Fiber morphology	Medium				Medium	
OP-100 lubricant	1%	1%	2%	2%		
Talc					0%	7%
Zn-st					2%	2%
EBS					1%	1%
MAPE	0%	2%	0%	2%	–	–

HDPE, high density polyethylene; Talc, magnesium silicate hydroxide; OP-100, ester stearate lubricant; Zn-st, zinc stearate; EBS, ethylene bis stearamide; MAPE, polyethylene-maleic anhydride. Percentages are based on the oven dry weight of fibers.

(EBS) wax (GE Specialty Chemicals). Talc used was magnesium silicate hydroxide.

A 20 kg batch of each composite formulation (Table 1) was mixed in a drum blender for 10 min. The mixture was then conveyed to the feed hopper of a 55 mm counter-rotating conical twin-screw extruder (Cincinnati Milacron, Batavia, OH, USA) with front/rear diameter of 55/114 mm and length over diameter ratio of 22. Barrel length was 113 cm and dwell time was approximately 10 min. A slit die measuring 15.25 cm by 1.25 cm was attached to the extruder. During extrusion, temperatures of barrel/screw and die were 163 and 171 °C and screw rotational rate was 6–7 rpm and 10–12 rpm for black spruce and trembling aspen bark/HDPE composites, respectively. RPM speed and temperature for each composite were adjusted according to the species, fiber proportions and dimensions to obtain homogeneous composites with no apparent thermal degradation. After exiting the die, the extrudate sized 1.5 in. × 0.375 in. (38.1 mm × 9.5 mm) was spray-cooled with water and air at 20 °C.

2.5. Specimen preparation and determination of mechanical properties

For all tests, extruded samples were planed to 6.4 mm thickness. Specimens were cut from planed material and conditioned at 20 ± 3 °C and 65 ± 1% for mechanical evaluation. Flexural properties, including modulus of elasticity (MOE) and modulus of rupture (MOR) in static bending, and tensile properties, including strength at maximum load, modulus of elasticity, toughness, and strain at failure, were determined. Flexural properties were measured according to ASTM D 790 Test Method I. Three-point bending tests were conducted on 136.6 mm × 21.8 mm × 6.4 mm samples. The support span was 102.4 mm, resulting in a span-to-depth ratio of 16. The cross head speed was 2.73 mm/min. An MTS hydraulic test machine with 5 kN capacity was used for load application, displacement measurement, and data acquisition. Calculation of the MOE was based on the values obtained at 20–40% of maximum load in the load–displacement curves corresponding to the most linear portion of the curves. The ASTM D 638 Standard Test Method was used to determine tensile strength at maximum load and toughness, defined as the material's capacity to deform plastically and to absorb energy before failure.

2.6. Experimental design and data analyses

Factorial designs were used, with bark state (untreated and treated), bark fiber content (50 and 60%), and bark fiber size (fine: 0.19–0.25 mm, medium: 0.25–0.50 mm, and coarse: 0.50–1.00 mm) as the main factors for each species. This resulted in 12 combinations with 3 replicates, for a total of 36 extrudates for each bark species.

SAS 9.1 was used for the statistical analyses. Analysis of variance (ANOVA) and factorial contrasts were performed at 12 levels. When there was significant interaction between bark state and one or both of the two other factors, the values of those factors were fixed in the SAS model using the SLICE option of the LSMEANS procedure to assess the effect of hot water treatment (bark state) on the properties of bark thermoplastic composites made with black spruce and trembling aspen bark (Winer, 1971). Interaction curves of factors are provided.

Furthermore, the effects of the addition of different contents of coupling agent (MAPE) and lubricants (OP-100, talc) on composite properties were evaluated. Finally, the effect of different fiber nature (untreated and treated black spruce and trembling aspen bark) on the properties of manufactured composites was investigated.

3. Results and discussion

3.1. Bark extractive contents

Bark organic and inorganic extractive contents of both untreated and treated raw black spruce and trembling aspen bark are presented in Table 2. Significant differences are observed between the denatured ethanol solubility of untreated and treated bark of both species. A significant difference is also seen between the hot water solubility of untreated and treated trembling aspen bark. A comparison between the total extractive content of untreated and treated raw bark of each species (Table 2) shows that hot water treatment resulted in the removal of 6.9 and 11.2% of extractives from black spruce and trembling aspen bark, respectively. Nevertheless, the hexane solubility indicates no significant effect of hot water treatment on the lipophilic extractives of the two species. Both untreated and treated trembling aspen bark show higher lipophilic content than black spruce bark.

Table 2
Raw bark organic and inorganic extractive content.

	Black spruce bark (BSB)		Trembling aspen bark (TAB)	
	Untreated (%)	Treated (%)	Untreated (%)	Treated (%)
Successive extractions				
Hexane	3.4 (0.2)	3.6 (0.1)	6.5 (0.1)	6.6 (0.3)
Denatured ethanol	9.0 (0.3)	3.6 (1.5)	6.5 (0.1)	2.4 (0.1)
Hot water	9.4 (1.3)	7.7 (0.1)	13.3 (0.7)	6.1 (1.6)
Total	21.8	14.9	26.3	15.1
Direct hot water extraction	12.7 (0.6)	11.5 (2.8)	17.7 (0.4)	10.2 (0.2)
Ash	1.8 (0.1)	1.9 (0.1)	5.1 (0.4)	5.4 (0.5)

Standard deviation is in parentheses.

3.2. Effect of hot water treatment on bark/HDPE composites

Table 3 shows the bark fiber size categories obtained by screening. Mean length and width of each size category were obtained using the FQA. Fine fibers of each bark type show the smallest length/diameter (L/D) ratio and coarse fibers the greatest. For similar size category, L/D of untreated fibers is higher than that of treated fibers. Results on the impact of bark fiber content and size on the mechanical properties of the bark/HDPE composites were presented and discussed in a previous report (Yemele et al., 2010).

ANOVA results on the impact of hot water treatment of raw bark on the flexural and tensile properties of bark/HDPE composites are presented in Tables 4 and 5. A significant effect of bark state is observed on some flexural and tensile properties of bark/HDPE composites, except for the flexural MOR and MOE of BSB composites and the toughness and strain of composites made with TAB, where the difference between treated and untreated are not significant at 0.05 probability level. A significant effect of the interaction between bark state, bark content, and fiber size is also found on the flexural and tensile properties of bark/HDPE composites. This suggests that the effect of bark state depends on bark content and fiber size. When the interaction between bark state and the other factors (bark content and fiber size) is decomposed using the SLICE procedure in SAS, a significant effect of bark state is found on several combinations of bark content and fiber size category (Tables 4 and 5).

Comparisons between flexural and tensile properties of composites made with hot water treated and untreated bark fibers are summarized in Table 6. The applied treatment appears insufficient to significantly lower the flexural properties of composites made with BSB. Similarly, toughness and strain at failure of composites made with TAB are not significantly affected. In general, it has been reported that removing extractives from wood results in decreased mechanical properties and increased diffusion coefficient of WPC, with some exceptions, such as WPC made with pine (Kim et al., 2009).

3.3. Effect of MAPE, lubricant (OP-100) and talc on the properties of bark/HDPE composites

Table 7 shows a significant impact of the addition of talc on the properties of bark/HDPE composites, except for flexural MOR. Composites made without talc shows higher toughness and strain but lower flexural and tensile strength compared to those made with talc. The addition of talc (7%) results in increased flexural MOE, strength, and tensile MOE of the composites by 48%, 4%, and 23%, respectively. At the same time, it reduces toughness and strain by 48% and 43%, respectively.

The addition of lubricant (OP-100) and coupling agent (MAPE) significantly affect the flexural and tensile properties of bark/HDPE composites (Table 8). Higher mechanical resistance or modulus of elasticity (MOR, MOE, and tensile strength) and lower toughness and strain are obtained when a combination of 2% of OP-100 and 2% of MAPE is used. The addition of 1% lubricant and 2% coupling agent results in lower modulus of elasticity, toughness and strain.

ANOVA results of the interaction of lubricant (OP-100) and fiber types show that the properties of composites made with BSB generally decrease with increased OP-100 content (from 2.4 to 2.7%). In contrast, the properties of composites made with TAB are not significantly affected.

Table 3
Size of untreated and treated black spruce and trembling aspen bark fibers.

Fiber type	Fiber size category	Fiber size				
		Screen size		FQA		
		mm	Mesh	L (mm)	D (μm)	L/D
BSB untreated	Fine	0.18–0.25	80–60	0.34	38.40	8.85
	Medium	0.25–0.50	60–32	0.36	38.10	9.45
	Coarse	0.50–1.00	32–16	0.56	40.50	13.83
BSB treated	Fine	0.18–0.25	80–60	0.25	36.00	6.94
	Medium	0.25–0.50	60–32	0.50	37.00	13.51
	Coarse	0.50–1.00	32–16	0.54	35.90	15.04
TAB untreated	Fine	0.18–0.25	80–60	0.18	47.00	3.83
	Medium	0.25–0.50	60–32	0.24	42.80	5.61
	Coarse	0.50–1.00	32–16	0.41	38.40	10.68
TAB treated	Fine	0.18–0.25	80–60	0.21	42.60	4.93
	Medium	0.25–0.50	60–32	0.35	40.80	8.58
	Coarse	0.50–1.00	32–16	0.54	33.80	15.98

BSB, black spruce bark; TAB, trembling aspen bark; FQA, fiber quality analyzer; L, mean length; D, mean diameter.

Table 4
ANOVA results (*F*- and *p*-values) of the effect of hot water treatment (bark state) on the properties of black spruce bark/HDPE composites.

Source of variation	Flexural properties		Tensile properties			
	MOR	MOE	Strength	MOE	Toughness	Strain
Bark state (BS)	0.12 (0.73)	0.39 (0.53)	130.59 (<0.0001)	15.92 (<0.01)	165.95 (<0.0001)	124.92 (<0.0001)
(1) BS × BC	3.35 (0.08)	6.85 (<0.05)	22.42 (<0.0001)	9.05 (<0.01)	37.04 (<0.0001)	18.79 (<0.01)
(2) BS × FS	4.91 (0.02)	9.87 (<0.01)	25.86 (<0.0001)	6.66 (<0.01)	12.94 (<0.01)	15.61 (<0.0001)
(3) BS × BC × FS	4.56 (0.02)	–	22.02 (<0.0001)	8.64 (<0.01)	58.54 (<0.0001)	58.26 (<0.0001)
	(1) Sliced by BC					
50		1.98 (0.17)				
60		5.26 (0.03)				
	(2) Sliced by FS					
Fine		3.09 (0.09)				
Medium		6.57 (0.02)				
Coarse		10.47 (<0.01)				
	(3) Sliced by BC × FS					
50% fine	7.32 (<0.05)	–	139.88 (<0.0001)	0.01 (0.92)	17.55 (<0.01)	1.08 (0.31)
50% medium	7.79 (0.01)		19.21 (<0.01)	48.96 (<0.0001)	280.64 (<0.0001)	247.81 (<0.0001)
50% coarse	3.64 (0.07)		12.86 (<0.01)	2.17 (0.15)	5.24 (<0.05)	4.91 (<0.05)
60% fine	2.50 (0.13)		14.01 (<0.01)	3.28 (0.08)	28.04 (<0.0001)	25.16 (<0.0001)
60% medium	1.16 (0.2918)		8.51 (<0.01)	0.15 (0.70)	0.50 (0.48)	0.03 (0.87)
60% coarse	0.00 (1.0000)		54.31 (<0.0001)	1.00 (0.33)	13.97 (<0.01)	12.46 (<0.01)

BS, bark state; BC, bark fiber content; FS, fiber size; MOR, modulus of rupture; MOE, modulus of elasticity. *p*-values are in parentheses.

Table 5
ANOVA results (*F*- and *p*-values) of the effect of hot water treatment (bark state) on the properties of trembling aspen bark/HDPE composites.

Source of variation	Flexural properties		Tensile properties			
	MOR	MOE	Strength	MOE	Toughness	Strain
Bark state (BS)	5.88 (0.02)	58.77 (<0.0001)	70.65 (<0.0001)	16.10 (<0.01)	1.88 (0.18)	0.19 (0.67)
(1) BS × BC	9.18 (<0.01)	4.02 (0.06)	71.80 (<0.0001)	20.56 (<0.0001)	0.98 (0.33)	7.94 (<0.01)
(2) BS × FS	8.77 (<0.01)	7.62 (<0.01)	94.33 (<0.0001)	22.12 (<0.0001)	2.47 (0.10)	8.17 (<0.01)
(3) BS × BC × FS	–	–	223.68 (<0.0001)	14.19 (<0.0001)	–	–
	(1) Sliced by BC					
50		14.87 (<0.01)				2.84 (0.10)
60		0.18 (0.67)				5.29 (0.03)
	(2) Sliced by FS					
Fine	3.89 (0.06)	1.81 (0.19)			0.01 (0.75)	12.61 (<0.01)
Medium	12.77 (<0.01)	44.58 (<0.0001)			6.72 (0.02)	2.11 (0.16)
Coarse	6.75 (0.02)	27.61 (<0.0001)			0.10 (0.92)	1.81 (0.19)
	(3) Sliced by BC × FS					
50% fine			21.01 (<0.0001)	0.06 (0.81)		
50% medium			10.52 (<0.01)	1.32 (0.26)		
50% coarse			1.58 (0.22)	4.15 (0.053)		
60% fine			710.79 (<0.0001)	4.04 (0.06)		
60% medium			0.01 (0.91)	93.38 (<0.0001)		
60% coarse			34.58 (<0.0001)	7.92 (<0.01)		

BS, bark state; BC, bark fiber content; FS, fiber size; MOR, modulus of rupture; MOE, modulus of elasticity. *p*-values are in parentheses.

Table 6
Effect of hot water treatment of raw bark on the properties of bark HDPE composites.

Properties	HDPE composites with		Treated vs. untreated[a]	HDPE composites with		Treated vs. untreated[a]
	BSB untreated	BSB treated		TAB untreated	TAB treated	
Flexural						
MOR (MPa)	23.7	23.6	NS	21.4	20.8	−Y
MOE (MPa)	2323	2303	NS	1761	1605	−Y
Tensile						
Strength (MPa)	15.2	16.1	+Y	13.6	14.1	+Y
MOE (MPa)	2276	2222	−Y	1827	1782	−Y
Toughness (J/m^2)	15.6	18.7	+Y	22.3	22.9	NS
Strain (%)	1.48	1.66	+Y	2.24	2.23	NS

BSB, black spruce bark; TAB, trembling aspen bark; NS, not significant at 0.05 probability level. +Y: significant increase ($\alpha = 0.05$) between treated and untreated bark/HDPE composites; −Y, significant decrease ($\alpha = 0.05$) between treated and untreated bark/HDPE composites.

[a] Comparison between HDPE composites made with treated and untreated bark.

Table 7
Effect of talc on the properties of bark plastic composites.

Properties	Composites made with	
	0% talc	7% talc
Flexural		
MOR (MPa)	16.4^{A} (0.3)	17.3^{A} (0.1)
MOE (MPa)	1436^{A} (36)	2128^{B} (6)
Tensile		
Strength (MPa)	10.6^{A} (0.0)	11.0^{B} (0.0)
MOE (MPa)	1766^{A} (6)	2185^{B} (10)
Toughness (J/m^2)	24.1^{A} (0.3)	12.4^{B} (0.2)
Strain (%)	2.79^{A} (0.40)	1.56^{B} (0.02)

Standard error is in parentheses. Different letters within a line indicate a statistically significant difference ($\alpha = 0.05$) between the properties of composites.

Table 8
Effect of lubricant and coupling agent on the properties of bark/HDPE composites.

	F- and *p*-values					
	MOR	MOE	Strength	MOE	Toughness	Strain
OP-100	25.54 (<0.01)	12.55 (<0.01)	53.06 (<0.01)	18.98 (<0.01)	47.34 (<0.01)	9.42 (0.02)
MAPE	3.57 (0.09)	11.50 (<0.01)	11.69 (<0.01)	0.06 (0.81)	199.87 (<0.0001)	164.39 (<0.0001)
OP-100 × MAPE	26.05 (<0.01)	36.12 (<0.01)	90.52 (<0.0001)	30.23 (<0.01)	14.62 (<0.01)	0.51 (0.49)

OP-100 (%)	MAPE (%)	Mean value and standard error (in parentheses)					
		MOR (MPa)	MOE (MPa)	Strength (MPa)	MOE (MPa)	Toughness (J/m^2)	Strain (%)
1	0	17.8 (0.2)	1599 (12)	11.3 (0.0)	1866 (24)	21.2 (1.0)	2.41 (0.10)
1	2	16.4 (0.6)	1491 (58)	10.0 (0.4)	1553 (106)	10.8 (0.4)	1.59 (0.08)
2	0	17.8 (0.5)	1498 (53)	10.8 (0.0)	1804 (2)	23.0 (0.3)	2.67 (0.03)
2	2	20.9 (0.3)	1886 (22)	13.7 (0.1)	2090 (6)	17.0 (0.2)	1.75 (0.01)

p-values are in parentheses.

Table 9
Effect of different type of filler on the properties of bark/HDPE composites.

Properties	HDPE composites made with bark from	
	Black spruce (BSB)	Trembling aspen (TAB)
Flexural		
MOR (MPa)	21.3^{A} (0.3)	17.3^{B} (0.1)
MOE (MPa)	2745^{A} (24)	2128^{B} (6)
Tensile		
Strength (MPa)	13.2^{A} (0.0)	11.0^{B} (0.0)
MOE (MPa)	2357^{A} (2)	2185^{B} (10)
Toughness[a] (J/m^2)	11.8^{A}(0.0)	12.4^{A} (0.2)
Strain[a] (%)	1.27^{A}(0.00)	1.56^{B} (0.02)

Standard error is in parentheses. Different letters within a line indicate a statistically significant difference ($\alpha = 0.05$) between the properties of the composites. Results presented in this table are for bark/HDPE composites of the following formulation: bark fibers of medium size (58%), HDPE (32%), Zn-st (2%), EBS (1%), and Talc (7%).
[a] At failure.

3.4. Effect of fiber nature on the properties of HDPE composites

The type of fiber used as filler significantly impacts the properties of HDPE composites (Table 9), in agreement with previous reports (Yemele et al., 2010; Bouafif et al., 2009a). Black spruce bark (BSB) composites exhibit higher mechanical properties than trembling aspen bark (TAB) composites, with the exception of toughness and strain. These results are in agreement with previous work (Yemele et al., 2010), where different stress–strain behaviors were obtained between composites made with BSB and TAB.

4. Conclusions

The effects of hot water treatment of raw bark and the addition of coupling agent (MAPE) and lubricants (OP-100) on the flexural and tensile properties of bark/HDPE composites were investigated. Results showed a significant impact of hot water extraction on flexural and tensile properties of bark/HDPE composites, with the exception of the flexural modulus of rupture and modulus of elasticity of black spruce bark (BSB) composites and the tensile toughness and strain of trembling aspen bark (TAB) composites. However, when significant, the impact of hot water extraction on the mechanical properties of both BSB and TAB composites remained small. Bark extracts highly desired in pharmacology and adhesive production could be removed and the remaining residues used to manufacture composites. Lubricant and coupling agents used significantly improved the strength properties of the composites and reduced toughness and strain. HDPE/bark composites showed higher modulus of elasticity with the addition of 2% of OP-100 and 2% of MAPE.

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