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Manuel Raul Pelaez-Samaniego, Vikram Yadama*, Eini Lowell, Thomas E. Amidon and Timothy L. Chaffee

Hot water extracted wood fiber for production of wood plastic composites (WPCs)

Abstract: Undebarked ponderosa pine chips were treated by hot water extraction to modify the chemical composition. In the treated pine (TP), the mass was reduced by approximately 20%, and the extract was composed mainly of degradation products of hemicelluloses. Wood flour produced from TP and unextracted chips (untreated pine, UP) was blended with high-density polyethylene (HDPE) and polypropylene (PP) and was extruded into wood plastic composites (WPCs). Formulations for WPCs consisted of 58% pine, 32% plastic, and 10% other additives. WPC based on HDPE+TP and PP+TP absorbed 46–45% less water than did WPC based on HDPE+UP and PP+UP, respectively. Thickness swelling was reduced by 45–59%, respectively, after 2520 h of immersion. The diffusion constant decreased by approximately 36%. Evaluation of mechanical properties in flexure and tension mode indicated improvements in TP-WPC properties, although the data were not statistically significant in all cases. Results showed that debarking of ponderosa pine is not required for WPC production.

Keywords: extrusion, hot water extraction, hygroscopicity, wood plastic composites (WPC)

***Corresponding author: Vikram Yadama,** Composite Materials and Engineering Center, Washington State University, Pullman, WA 99164 USA, Phone: +(509) 335-6261, e-mail: vyadama@wsu.edu
Manuel Raul Pelaez-Samaniego: Biological Systems Engineering Department, Washington State University, Pullman, WA, USA; and Faculty of Chemical Sciences, Universidad de Cuenca, Cuenca, Ecuador
Vikram Yadama: Department of Civil and Environmental Engineering, Washington State University, Pullman, WA, USA
Eini Lowell: USDA Forest Service, Pacific Northwest Research Station, Portland, OR, USA
Thomas E. Amidon: Department of Paper and Bioprocess Eng., State University of New York, Syracuse, NY, USA
Timothy L. Chaffee: Ashland Inc., Ashland Hercules Water Technologies, Madison, WI, USA

Introduction

Wood fiber is a renewable material that serves traditionally for manufacturing a variety of composites. If not protected, wood and wood fibers are susceptible to water uptake and fungal decay; thus, protecting wood constituents in a composite from moisture is mandatory in exterior applications. Wood plastic composites (WPCs) have gained popularity due to their superior outdoor durability (Clemons 2002; Morrell et al. 2010). However, the surface quality of WPCs also deteriorates considerably, as demonstrated by accelerated weathering in laboratory (Cameron 2009) or under outdoor conditions (Kiguchi et al. 2007). Moisture infiltration into wood fibers in WPCs causes their swelling, which stresses the interfacial bond between fibers and plastic. Thus, the strength of the composite as a whole is weakened (Stark 2001). Repeated swelling and shrinking over time eventually lead to microcracks in the composite, which serve as pathways for decay fungi and mould. The strength and stiffness values of WPCs also decrease in experiments when they are exposed to accelerated freeze-thaw cycling in laboratory testing. Again, water penetrates into the composite, entailing bonding deterioration between wood and plastic (Panthapulakkal et al. 2006; Pilarski and Matuana 2006; Cameron 2009). Accordingly, an option to reduce the effect of water is to improve wood characteristics through processes that modify its chemical structure.

Thermal and chemical treatments improve the durability of wood (Hill 2006; Rowell 2007). The former was found to reduce wood's hygroscopicity, increase the degree of crystallinity of cellulose, and improve dimensional stability and resistance to fungal degradation (Bhuiyan et al. 2000; Kamdem et al. 2002; Rowell et al. 2009; Stanzl-Tschegg et al. 2009; Windeisen et al. 2009; Pfriem et al. 2010; Dubey et al. 2012). Impregnation of wood with chemicals is also effective (Spindler et al. 1973; Schneider 1994; Dieste et al. 2009; Hill et al. 2009; Bryne and Wålinder 2010; Chirkova et al. 2011; Xiao et al. 2012). However, this option is not always viable for economical and environmental reasons, as chemicals or solvents are expensive and require special handling and disposal.

Hot water extraction (HWE) removes sugars and other components from lignocellulosic materials. Hemicelluloses undergo degradation by autohydrolysis. HWE is conducted typically at 140°C–190°C without adding chemicals (Amidon et al. 2008). Under controlled conditions, the effect of HWE is restricted mainly to hemicelluloses removal, i.e., to the most hydrophilic constituent of wood (Skaar 1972).

HWE is of interest in the context of production of biofuels from lignocellulosic materials and in the context of the pulping industry (Amidon et al. 2008; Carvalheiro et al. 2008; Dautzenberg et al. 2011; Gütsch and Sixta 2011; Hörhammer et al. 2011; Kuhad et al. 2011; Testova et al. 2011). Moreover, HWE can be integrated into the production of wood composites (Andrusyk et al. 2008; Paredes et al. 2008; Hosseinaei et al. 2012). Andrusyk et al. (2008) showed that a two-step HWE process, performed at 95°C–160°C with a mix of hardwood chips, leads to increasing compatibility between wood and polypropylene (PP) in extruded WPCs. The mechanical properties of the products are not negatively affected. In the quoted study, however, the changes in hygroscopicity of the composites were not reported. Hosseinaei et al. (2012) investigated injection molded WPCs made of HWE-treated southern yellow pine (extraction at 140°C, 155°C, and 170°C during 60 min) and found reduced water absorption (WA) and increased tensile strength in the products. In both quoted works, wood was debarked.

The objectives of the present study were to (1) conduct HWE of undebarked pine chips and (2) analyze the effects of chemical and structure modification on processing and on the physical and mechanical properties of extruded WPCs.

Materials and methods

Small-diameter (<25 cm at breast height) ponderosa pine (*Pinus ponderosa*) trees were harvested from a forest site in central Oregon, where trees with a small diameter are removed (thinning) to reduce fire risk ("fuel reduction area", see Skog et al. 2006). Trees were bucked into logs (Figure 1) and converted into chips without debarking. Chips were subjected to an HWE process at 160°C for 90 min as described by Chaffee (2011). HWE removed 20% of the initial mass. The extraction mixture was analyzed by proton nuclear magnetic resonance (^{1}H NMR) spectroscopy and the quantification was accomplished by adding glucosamine as standard. The extraction mixture contained sugars (67.1%; for composition, see Figure 1), acetic acid (5.6%), inorganics (1.9%), other compounds (e.g., methanol, furfural, formic acid) (11.5%), and other unidentified components (13.9%) (Chaffee 2011).

The WPC extrusion was conducted with blends of unextracted and HWE pine chips; the plastic component was high-density polyethylene (HDPE) or PP homopolymer (PP) (Table 1). Both polymers were obtained from Bamberger Polymers, Houston, TX, USA. The

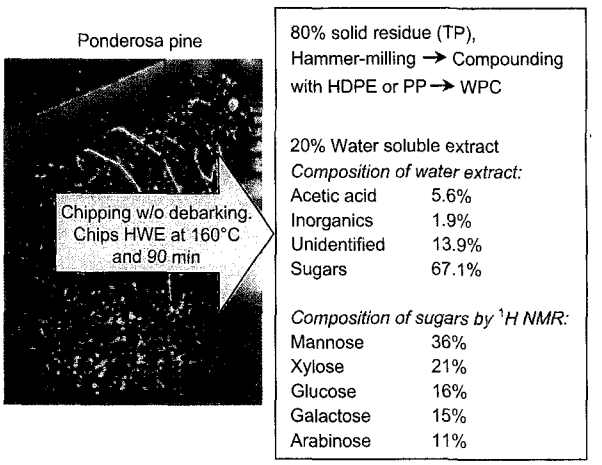

Figure 1 Ponderosa pine logs, outline of the experiments, and results of the HWE process.

density and melt flow index of HDPE (HP54-60) and PP (H04F-00) were 0.954 g cm^{-3} and 0.55 g/10 min at 190°C and 0.90 g cm^{-3} and 4.0 g/10 min at 230°C, respectively. WPC boards were produced with four combinations of materials: (1) untreated pine (UP) with HDPE (herein named as UP/HDPE), (2) HWE pine (referred to as treated pine, TP) with HDPE (TP/HDPE), (3) UP with PP (UP/PP), and (4) TP with PP (TP/PP).

Material preparation and analysis

HWE treated chips (TP) and control chips (UP) were converted into wood flour in a Bliss Industries hammer mill. Particle size distribution (as per ASTM D5644-01) and moisture content (ASTM D4442-07) were analyzed after grinding. Thermogravimetric analysis (TGA) (ASTM E1131-08) was performed in a simultaneous differential scanning calorimetry-TGA instrument (TA SDT Q600) to compare the thermal degradation of UP vs. TP in N_2 atmosphere (flow rate of 100 ml min^{-1}) in the range of 35°C–600°C at a heating rate of 10°C min^{-1}. The morphology of the TP and UP chips was investigated by means of an FEI Quanta 200F Scanning Electron Microscope (SEM). The effect of HWE on wood was qualitatively estimated by means of pyrolysis gas chromatography mass spectrometry (Py-GC/MS) (Qiang et al. 2009); the instrument used was an Agilent 6890N Network GC System, at 500°C. Identification of MS peaks was conducted based on the NIST/EPA/NIH Mass Spectral Library V. 2.0d (Fair Com Corp). The peaks in the pyrograms were normalized considering the dry mass employed in each test. Ion chromatography for sugar analysis (Lee 1990) was done according to ASTM D5896-96, using a *DIONEX ICS-3000* equipment.

Because the target WPC formulations were 60/40, rheology analysis, without additives, was conducted with 60% of UP or TP and 40% of HDPE or PP to compare the behavior during compounding. Blends were compounded for 10 min in a Haake Rheomix 600 torque rheometer equipped with roller-blade rotors, with 50 g of material of each formulation. Other rheometer parameters were as follows: screw speed of 20 rpm and temperatures of 160°C and 170°C (HDPE formulations) and 180°C and 190°C (PP formulations). These temperatures were chosen based on melting points of 140°C and 173°C for HDPE and PP, respectively, and the initiation of thermal degradation of wood after the TGA results.

	Composition of WPCs by weight					Extruder operating conditions		
WPC type	Wood (%)	Polymer (%)	Lubricant (%)[a]	ZB (%)	Talc (%)	Current intensity (A)	Melting pressure (MPa)	Melting temperature (°C)
UP/HDPE	58	32	3	2	5	8±0	3.3±0	162±1
TP/HDPE	58	32	3	2	5	6.7±0.5	4.4±0.1	163±0
UP/PP	58	32	3	2	5	5±0	3.2±0.1	185±0
TP/PP	58	32	3	2	5	5±0	3.7±0.1	187±0

Table 1 Wood plastic formulations and extrusion conditions.
ZB, zinc borate.
[a]2% of zinc stearate +1% of ethylene bis-stearamide.

Extrusion of WPC

The extruder operating conditions are summarized in Table 1. Materials were dry-blended for 10 min in a rotary drum mixer prior to being extruded using a 35-mm intermeshing twin-screw extruder (Cincinnati Milacron Inc.) equipped with a 37×10 mm cross-section die. Results from rheological tests and melting temperatures of HDPE and PP were considered in setting the extruder working temperature. The die temperatures were set at 175°C for HDPE and 190°C for PP formulations. Material was extruded at 20 rpm (as for rheology tests).

WA and dimensional stability analysis

Four replicates from each formulation were prepared to conduct long-term water absorption (WA) tests (4320 h of immersion) as per an adaptation (the specimens were of prismatic shape instead of discs) of ASTM D570-98 to determine moisture uptake and dimensional stability. All specimens were machined on the surfaces (using a Delta DC-80 planer) to remove approximately 1-mm thickness of their thermoplastic rich skin. Thus, the specimens' final dimensions were 70×36×8 mm^3. The surface roughness of the specimens was not quantified after machining. After this, the specimens were conditioned at 25°C and 55% of relative humidity (RH) for 48 h and weighed at a precision of 0.01 g, and their dimensions (length, width, and thickness) were measured at a precision of 0.01 mm. Specimens were then immersed into distilled water at room temperature.

WA was determined by dividing the weight increment per time t by the initial weight. Measurements of weight, thickness (at four equidistant points from the edges and three points covering the rest of the surface), width, and length (at two predetermined points equidistant from the edges in each case) were recorded after 24, 48, and 72 h and subsequently after 7, 14, 21, 28, 35, 49, 63, and 105 days from the time the test was started. After 105 days, warping of UP-WPC was observed, which affected the precision of the dimensional measurements. Thus, only weight was further measured until day 180, when the specimens were considered saturated. For the measurements, the samples were removed randomly from the water and blotted to remove excess water on surfaces. Swelling was determined as usual based on the corresponding initial dimensions. Water uptake until saturation was measured and the diffusion constant (D) were determined based on the data according to Rangaraj and Smith (2000). The interface between the filler and the matrix was observed by scanning electron microscopy (SEM) (FEI Quanta 200F equipment).

Mechanical tests

Six WPC specimens of each formulation (24 in total) were tested in flexure mode (ASTM D790-10) without altering the specimens' surfaces beyond cutting to the overall length of 200 mm. The specimens were conditioned for 72 h (T=25°C, 55% RH) and the specimens' densities were determined. Flexure testing was conducted using an Instron 4466 machine equipped with a 10 kN load cell; the support span was 20 times the depth of the beam and the crosshead motion was 4.3 mm min^{-1}.

Five Type III "dogbone" tensile specimens (overall length of 246 mm) for each formulation (20 specimens in total) were prepared according to ASTM D638-10. The specimens (conditioned similar to flexural specimens) were tested for tension in the same equipment used for the flexural tests; displacements in the necked down region was recorded with a 25-mm displacement extensometer (MTS 634.12E-24). The test speed was 5 mm min^{-1}. Analysis of variance (ANOVA) using SAS® Software (SAS, Cary, NC, USA; confidence level, α=0.05) was conducted to determine the statistical significance of the data.

Results and discussion

The color of the TP chips turned to dark brown in comparison with the UP chips. Color changes in thermally treated wood have been attributed to the oxidation of phenolic

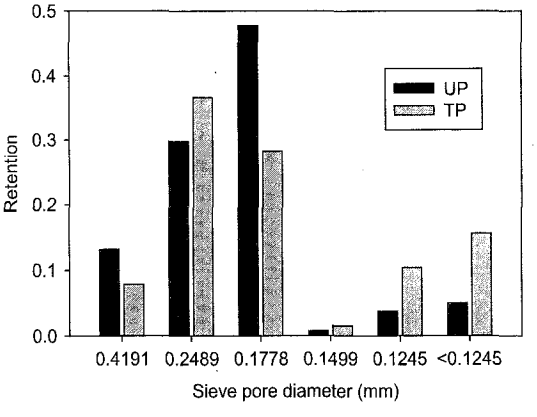

Figure 2 Particle size distribution.

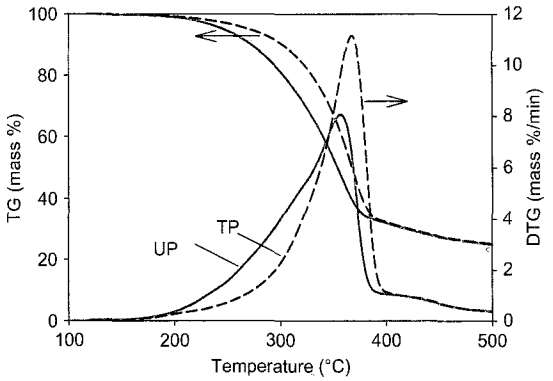

Figure 3 TG and DTG curves.

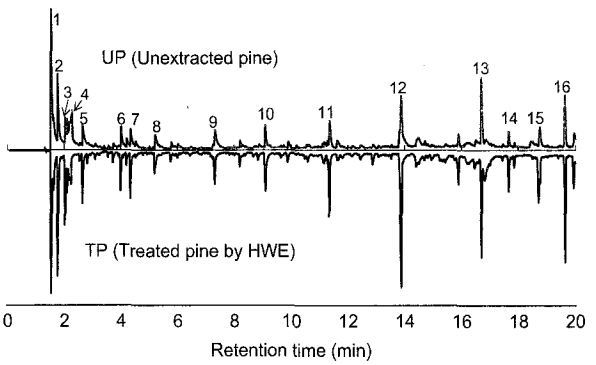

Figure 4 Comparison of Py-GC/MS chromatograms of UP and TP.

compounds, the presence of reduced sugars and amino acids, or the emanation of formaldehydes (Sandoval-Torres et al. 2010). Particle size distribution (Figure 2) shows that approximately 26% of TP and 9% of UP have a particle size equal to or less than 0.25 mm, indicating that TP contained almost three times the amount of fines than UP. HWE chips fractured more easily than the control chips during grinding, which can be attributed to the effect of thermal treatment. It is known that thermal modification makes wood brittle and elevates grindability (Bridgeman et al. 2010).

Thermogravimetry, Py-GC/MS, and rheology

The TG and differential thermogravimetry (DTG) results (Figure 3) show that UP started degrading at a lower temperature than TP did. In particular, 0.5%, 1%, and 2% of weight loss occurred at 191°C, 215°C, and 237°C, respectively, for UP, and at 209°C, 229°C, and 251°C, respectively, for TP. The degradation of UP occurred essentially in two major stages. The 1st one corresponded to degradation of hemicelluloses, and the 2nd, to that of cellulose. A 3rd stage (overlapped in the presence of cellulose and hemicelluloses), covering the whole range of conversion, was associated with lignin degradation (Órfão et al. 1999). The absence of the 1st stage in case of TP reveals that HWE has changed the composition of wood by removal of hemicelluloses.

Ion chromatography (Table 2) confirmed the extraction of hemicelluloses. In the same line are the results of Py-GC/MS (Figure 4 and Table 3). Analytical pyrolysis is an established method for the analysis of complex polymerized materials, including WPCs (Windt et al. 2011). This is the reason this method was applied for a rapid estimation of the effects of HWE. Based on the area of peak 4, the amount of acetic acid formed during the pyrolysis of TP was reduced by approximately 32%. Because acetic acid is formed mainly from hemicelluloses, their removal by HWE can be confirmed. In the pyrograms of TP, the intensities of the lignin-type peaks 11 (phenol) and 13 (2-methoxy-4-vinylphenol) were increased by 1.7 and 1.4 times, respectively. Accordingly, the relative content of lignin has been elevated in TP as a consequence of the removal of hemicelluloses. It was shown that cellulose

	Concentration (ppm)		
	UP	TP	Change (%)
Arabinose	1.637±0.037	0.143±0.013	−91.3
Galactose	1.757±0.042	0.518±0.027	−70.5
Mannose/xylose	7.628±0.236	5.166±0.307	−32.3
Glucose	18.604±0.479	23.082±1.491	+14.3

Table 2 Sugar composition of unextracted (UP) and extracted (TP) materials as determined by hydrolysis plus ion chromatography.

Peak number	Substance
1	Carbon dioxide (CO_2)
2	1-Propen-2-ol, acetate ($C_5H_8O_2$)
3	Acetaldehyde, hydroxy- ($C_2H_4O_2$)
4	Acetic acid (CH_3CO_2H)
5	2-Propanone, 1-hydroxy- ($C_3H_6O_2$)
6	1,2-Ethanediol, monoacetate ($C_4H_8O_3$)
7	Propanoic acid, 2-oxo-, methyl ester ($C_4H_6O_3$)
8	Furfural ($C_5H_4O_2$)
9	1,2-Cyclopentanedione ($C_5H_6O_2$)
10	Oxazolidine, 2,2-diethyl-3-methyl- ($C_8H_{17}NO$)
11	Phenol, 2-methoxy- ($C_7H_8O_2$)
12	Phenol, 2-methoxy-4-methyl- ($C_8H_{10}O_2$)
13	2-Methoxy-4-vinylphenol ($C_9H_{10}O_2$)
14	Eugenol ($C_{10}H_{12}O_2$)
15	Benzaldehyde, 4-hydroxy-3-methoxy- ($C_8H_8O_3$)

Table 3 Some chemical compounds in unextracted (UP) and extracted (TP) materials identified by Py-GC/MS (see Figure 3).

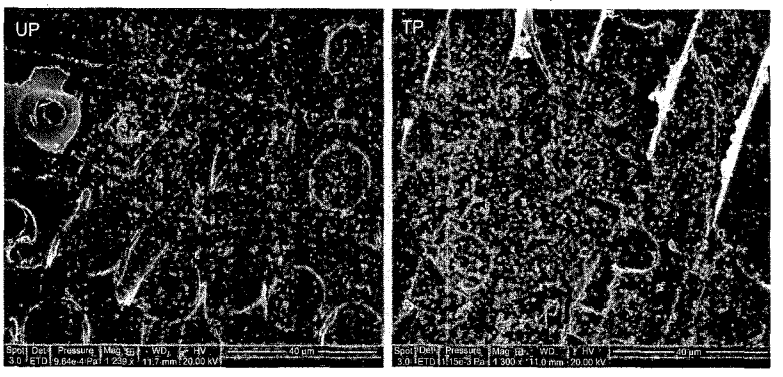

Figure 5 SEM images of control pine (UP) and hot-water extracted pine (TP).

and lignin are mostly retained in wood after HWE at 160°C (Amidon et al. 2008), as the hydrolytic degradation of cellulose begins at 200°C (Mok and Antal 1992).

The SEM micrographs of the chips (Figure 5) showed some small spherical-like droplets, which could be attributed to the coalescence and migration of lignin to the surface of cells and its condensation on the walls (Selig et al. 2007; Sannigrahi et al. 2011). Threads and elevated roughness on the fiber surfaces were observed, which certainly contributed to a better adhesion between fibers and the polymer matrix.

The results of the torque rheology tests indicated that (1) the peak torque (at loading conditions) was less for formulations based on TP and (2) the torque required when the blends reached their lowest viscosity (when the torque is stable) was approximately the same for both UP and TP, irrespective of the thermoplastic matrix. The results suggest that the torque required for extrusion was either reduced or not affected as a consequence of wood modification by HWE. This could potentially influence the energy consumption during the manufacturing process.

WPC properties

The densities of the boards were similar for UP/HDPE and TP/HDPE (1.18±0.03 g cm^{-3}) and for UP/PP and TP/PP (1.10±0.01 g cm^{-3}). The densities of formulations containing HDPE were comparable with the densities of WPC boards obtained in a previous work with commercial wood flour (1.153 g cm^{-3}) (Yadama et al. 2009). The WA of WPCs produced with TP was significantly less than that of those produced with UP (Figure 6a). In particular, TP/HDPE boards absorbed 12.2% and TP/PP boards absorbed 12.5% of water after 2520 h of immersion, while both UP/HDPE and UP/PP formulations absorbed approximately 23% of water, with a reduction in water uptake of over 45% in both cases. WPCs manufactured with similar formulations, except with commercially produced pine wood flour, absorbed 18% of water after 672 h of immersion (Yadama et al. 2009); WPC specimens in this study absorbed 14%, 11%, 6%, and 5.9% water for UP/HDPE, UP/PP, TP/HDPE, and TP/PP formulations, respectively, after 672 h of water immersion. The significant reduction in moisture uptake in WPC specimens produced with HWE wood flour, irrespective of the type of matrix, is due to

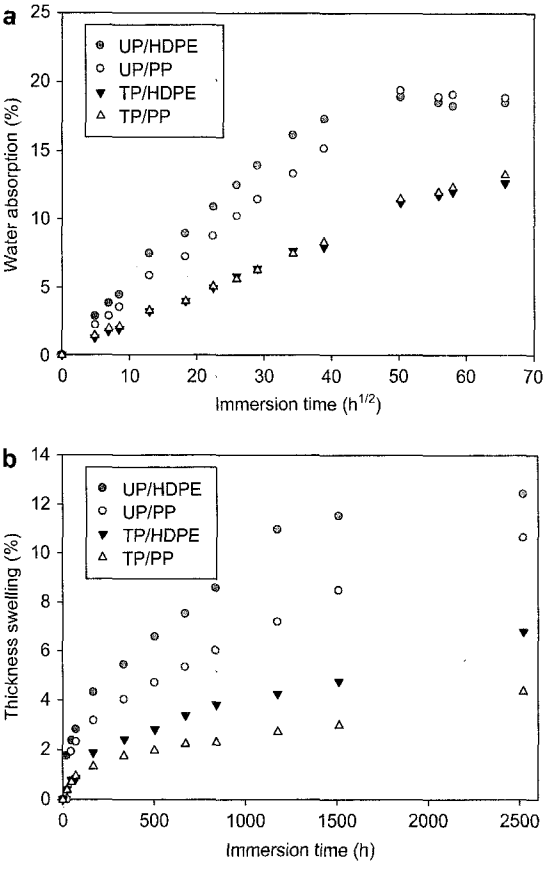

Figure 6 Properties of WPCs: (a) WA and (b) TS.

WPC	Flexural data		Tensile strength (MPa)	Young's modulus (E) (GPa)
	MOR (MPa)	MOE (GPa)		
UP/HDPE	27.59 (2.2) A	3.77 (7.2) A	14.46 (2.7) A	3.89 (13.5) A
TP/HDPE	31.70 (3.8) B	3.75 (5.7) A	16.52 (1.5) B	4.60 (11.4) A
UP/PP	28.50 (9.6) A	3.62 (4.0) A	15.67 (3.9) A	3.58 (11.8) A
TP/PP	32.20 (8.5) B	3.69 (4.9) A	15.36 (3.4) A	3.59 (18.9) A

Table 4 Results of the flexural and tension tests.
For each property, comparison of means was conducted between the wood treatments for each thermoplastic matrix.
Values in parenthesis are the corresponding coefficients of variation (%).
Values with different letters indicate significant differences at the α=0.05 level.

removal of large parts of hygroscopic hemicelluloses with their accessible OH groups (Skaar 1972; Rowell 2007).

The plot "water uptake of WPC vs. the square root of time" (Figure 6a) shows an initial linear relationship with eventual plateauing upon saturation (after 180 days of immersion); thus, a simple diffusion model can be applied to predict WA. Therefore, the diffusion constant (D) was predicted by Fick's law of diffusion. The values of D obtained were as follows: 0.000244, 0.000257, 0.000155, and 0.000164 $mm^2 s^{-1}$ for UP/HDPE, UP/PP, TP/HDPE, and TP/PP, respectively, showing that the D of formulations based on TP decreased by approximately 36% for both HDPE and PP formulations.

The degree of interfacial adhesion between the fibers of TP and UP and PP matrix was assessed qualitatively by investigating the fiber-matrix gap visible in SEM images. The low gap size between the TP fibers and matrix indicated a decreasing moisture uptake due to reduced capillary action. This observation can also be interpreted as the manifestation of increased porosity of TP fibers (Kobayashi et al. 2009), facilitating a better penetration of the plastic.

WPCs produced with TP revealed lower thickness swelling (TS) (Figure 6b), linear expansion (LE), and change in width (δW). After 2520 h of immersion, TS was reduced by 45–59% for TP-HDPE and TP-PP formulations, respectively. In general, LE was not higher than 2.2%, but TP-WPCs showed an LE reduction of more than 40%, irrespective of the matrix. Similarly, δW was reduced by 42% and 36% for HDPE and PP, respectively. These results reflect the change in hygroscopicity of cell wall material due to chemical structure modification during HWE.

The flexural strength (modulus of rupture, MOR) of TP/HDPE was increased by approximately 15%, and that of TP/PP, by approximately 13% (Table 4). Both results were statistically significant, as indicated by ANOVA and comparison of means analysis at α=0.05. The increase in flexural modulus (modulus of elasticity, MOE) was not statistically significant for TP-WPCs (Table 4). Statistically, there was a significant difference (14%) between the tensile strength of formulations based on UP and TP with HDPE; however, as with MOE, an increase in Young's modulus, E, was not statistically significant in the case of TP-HDPE and TP-PP. In comparison, the MOE of the WPC specimens extruded with commercial pine flour was approximately 4.3 GPa, and MOR was approximately 22 MPa (Yadama et al. 2009).

Conclusions

Hot water extracted (HWE) undebarked ponderosa pine significantly enhanced the moisture resistance of both PP- and HDPE-based WPCs. It can be safely concluded that HWE has a positive impact on WPC quality. The mechanical properties of TP-WPCs were either unchanged or even significantly better than those prepared with UP. The removal of hemicelluloses by HWE also opens the possibility for versatile utilization of the isolated hemicelluloses as value-added products.

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