EFFECT OF EXTRACTIVES ON WATER SORPTION AND DURABILITY OF WOOD–PLASTIC COMPOSITES

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(Received February 2009)

Abstract. Wood–plastic composites (WPCs) were made from isotactic polypropylene and extracted and unextracted flours of one of four different wood species. WPCs made with extracted wood flour had lower mechanical properties than unextracted WPCs with the exception of pine WPCs. For all of the species except pine, WPCs made with extracted wood flours showed higher moisture sorption and thickness swelling characteristics. Higher levels of fungal decay were observed for the WPCs made with extracted wood, except for the pine WPCs, in which there was lower fungal decay from brown rot in the extracted wood samples. These results demonstrate that wood extractives affect the mechanical properties, water sorption, and fungal decay resistance of WPCs.

Keywords: Wood–plastic composites, extractives, mechanical properties, water sorption, fungal durability.

INTRODUCTION

Wood–plastic composites (WPCs) use low-cost, lightweight wood flour as a filler or reinforcement in a thermoplastic matrix. Since their appearance in the market, WPCs have been used in decking, railing, window frames, doors, and auto parts. Unlike inorganic fillers such as calcium carbonate and talc, wood is susceptible to biological degradation. Currently, about two-thirds of WPCs produced are used in outdoor exposure such as decking and railing (Wolcott et al 2005). This can lead to deterioration of the WPCs by biotic (fungi and mold) and abiotic (moisture, sunlight, and temperature) agents (Morris and Cooper 1998; Rangaraj and Smith 2000; Lundin 2001; Silva et al 2001; Verhey et al 2001; Pendleton et al 2002; Dawson-Andoh et al 2004; Schirp and Wolcott 2005; Morrell et al 2006; Manning and Ascherl 2007).

Wood is a biodegradable composite of cellulose, hemicelluloses, lignin, and extractives. Extractives are nonstructural components that can be removed with organic solvents or water (Hillis 1970; Koch 1985; Sjöström 1993). A large number of the compounds in extractives have been identified, including terpenes, aliphatic compounds (mainly fats and waxes), and phenolics (Koch 1972; Rowe and Coner 1979; Fengel and Wegener 1984). However, the content and composition of extractives vary greatly among species, within species, and even within trees

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(Taylor et al 2002). For most tree species growing in temperate forests, extractives make up 2 – 10% of the dry wood mass (Koch 1972; Fengel and Wegener 1984). The molecular mass of extractives range from volatile low-molecular-weight compounds to high-molecular-weight polymers (Sjöström 1993).

Extractives in the heartwood of some species increase woods resistance to biological degradation (Wang and Hart 1983; Schultz et al 1995; Schultz and Nicholas 2000; Taylor et al 2002, 2006; Liu 2004). Extractives also affect surface chemistry, moisture sorption, and swelling properties of wood (Mantanis et al 1994, 1995; Choong and Achmadi 1991; Nzokou and Kamdem 2004, 2005). In general, extracted wood sorbs more moisture than unextracted wood at high RH because of the increased availability of moisture sites previously occupied by extractives (Spalt 1957; Wangaard and Granados 1967; Choong and Achmadi 1991; Nzokou and Kamdem 2004). The maximum swelling and wood swelling rate of extracted wood is also higher than unextracted wood (Stamm and Loughborough 1942; Nayer 1948; Wangaard and Granados 1967; Mantanis et al 1995). Mantanis et al (1995) suggested that such increases may be from faster diffusion of swelling liquid into the wood and increased chemical reactivity of the swelling liquid toward the various wood polymers that have been freed of extractives.

Recent work has demonstrated that WPCs made with wood species with high natural durability (eg eastern redcedar, black cherry, and Osage orange) are more resistant to biological degradation than WPCs made with susceptible wood species (Kim et al 2008). The increased fungal decay and mold resistance of these WPCs could be from the presence of toxic extractives in the wood and/or the low moisture sorption characteristics of the WPCs made with those species.

Little has been reported of how the use of extracted wood affects mechanical properties of WPCs. Saputra et al (2004) prepared WPCs with pine and Douglas-fir wood flours that had been extracted using three different solvents (acetone/water, dioxane/water, and benzene/ethanol followed by ethanol). They found that the mechanical properties of the WPCs increased when extracted wood flour was used, except for the dioxane/water-extracted Douglas-fir WPCs. They suggested that increases in mechanical properties were from the increased interfacial strength between extracted wood and the polypropylene (PP) matrix by the removal of weak boundary layers formed by extractives.

To our knowledge, there are no data published on the influence of extractives on the water sorption and fungal durability of WPCs. The objective of this study was to investigate how the removal of extractives affects the mechanical properties, fungal durability, and water sorption characteristics of WPCs, including those made with durable wood species.

MATERIALS AND METHODS

Preparation of Wood Flour

Dry black cherry (*Prunus serotina*) and eastern redcedar (*Juniperus virginiana*) wood was purchased from local sources. Fresh-cut Osage orange (*Maclura pomifera*) was harvested from a small tree, transported to the laboratory, and air-dried. All the wood used was combined sapwood and heartwood. Wood of each species was ground using a hammer mill and Wiley mill followed by sieving with 70 and 120 US standard sieves (square openings of 0.210 and 0.125 mm per side, respectively). The wood flour passing the 70 sieve but remaining on the 120 sieve was used in the subsequent manufacture of WPCs. Southern pine (*Pinus* spp.) wood flour was obtained from American Wood Fibers (Schofield, WI). The pine wood flour comprised particles that passed a 60 US standard sieve that were further sieved using the same mesh sizes described to get a similar wood particle size distribution. Virgin isotactic PP homopolymer (generic brand; Performance Polymers, Leominster, MA) with a melt flow index of 35 g/10 min at 230°C was used as the matrix. Density at room temperature was 910 kg/m^3.

Removal of Extractives

Wood flours were extracted following ASTM D 1105-96 (ASTM 2007a). Approximately 25 g of oven-dried wood flour in a cellulose thimble (43 mm ID × 123 mm long) was placed in a Soxhlet apparatus. The wood was extracted 4 h using ethanol:toluene (1:2 v/v). The toluene was subsequently removed by washing with ethanol. The wood flour was further extracted 4 h with neat ethanol. Extraction with each solvent was carried out at a rate of approximately 8 siphons/h. The material was removed from the Soxhlet apparatus and air-dried 24 h. The extraction was completed using hot water for 4 h at 100°C with a change of water every 1 h. The wood was then air-dried for 24 h followed by oven-drying at 105°C. The percentage extractives removed was calculated as:

$$Ext(\%) = \frac{(W_0 - W_f)}{W_0} \times 100 \qquad (1)$$

where W_0 is the oven-dry mass of wood flour before extraction and W_f is the mass of the wood after extraction. Three replicates were made for each wood species. After extraction, the bulk density of both unextracted and extracted wood flour was calculated by measuring the volume of 5 g of oven-dried wood flour in a graduated cylinder. Three replicates were made for each sample.

Compounding and Sample Preparation

Each species of extracted and unextracted wood flour was compounded with PP at 50% by mass in a 27 mm corotating twin-screw extruder (Leistritz MICRO 27; American Leistritz Extruder Corp., Somerville, NJ) with a length-to-diameter ratio of 40:1. The barrel temperature of the extruder varied between 180 – 195°C and the screw speed was 30 rpm. The compounded material was immediately cooled in a water bath and subsequently pelletized. The pellets were used to make injection-molded tensile test specimens in accordance with ASTM D638 Type IV (ASTM 2007b). The barrel and mold temperatures of the pneumatic injection molder were 191 and 135°C, respectively.

Tensile Testing

The tensile strength and modulus of injection molded specimens were measured using a universal testing machine (Model 5567; Instron Inc., Canton, MA) following ASTM D638. Five replicates were made for each wood species used.

Water Sorption and Thickness Swelling

The injection-molded tensile specimens were cut and machined to samples measuring 25.0 × 21.0 × 2.5 mm. The surface of the samples was ground off using 100-grit sandpaper to expose wood fibers that were encapsulated in the plastic matrix. The sample mass and thickness were measured before soaking in distilled water at room temperature. The samples were periodically removed to measure mass gain and thickness swelling. For each treatment, five replicates were made for the water sorption test and three different spots on each specimen were measured for the thickness swelling test. After more than 1600 h (67 da) of immersion in water, the samples were oven-dried at 105°C for 48 h and weighed to calculate the water sorption and thickness swelling. Percentage mass gain (*MC*) and thickness swelling (*TS*) were calculated based on the following equations:

$$MC(\%) = \frac{(W_t - W_o)}{W_o} \times 100 \qquad (2)$$

$$TS(\%) = \frac{(T_t - T_i)}{T_i} \times 100 \qquad (3)$$

where W_o is the oven-dry mass and W_t is mass at time t, whereas T_i is initial thickness and T_t is thickness measured at time t. The moisture sorption of wood flours under controlled humidity and temperature conditions (20°C, 95% RH) was also calculated based on Eq 2. Approximately 3 g of wood flour was dried under vacuum (50°C, 85 kPa) for 24 h and placed in an aluminum pan (70 mm dia) to form a thin layer of wood flour. The wood flour samples were then placed in a humidity chamber and the mass gain was periodically measured.

The water sorption data of WPCs were used to calculate apparent diffusion coefficient, D_A, using Fick's diffusion equation:

$$D_A = \frac{\pi}{16}\left(\frac{h}{MC_{\max}}\right)^2\left(\frac{\partial MC}{\partial\sqrt{t}}\right)^2 \quad (4)$$

where $MC_{\max}$ is the maximum MC measured at the end of the test, $\partial MC/\partial\sqrt{t}$ is the slope taken from the MC vs the square root of time relation, and h is thickness of the sample (Steckel et al 2007). Because Eq 4 is one-dimensional, diffusion through the WPC sample edges was accounted for using a geometric edge correction factor that is given by:

$$ECF = \left(1 + \frac{h}{L} + \frac{h}{w}\right)^2 \quad (5)$$

where h, w, and L are the sample thickness, width, and length, respectively (Shen and Springer 1976). Therefore, the corrected diffusion coefficient, D, is calculated as

$$D = \frac{D_A}{ECF} \quad (6)$$

In addition to WPCs, bulk diffusion coefficients of wood flour (D_f) were also calculated as:

$$D_f = \frac{\pi h^2}{4}\left[\frac{\partial(MC_t/MC_{\max})}{\partial\sqrt{t}}\right]^2 \quad (7)$$

where h is the height of wood flour sample in an aluminum pan calculated based on the bulk density of wood flours and $\partial(MC_t/MC_{max})/\partial\sqrt{t}$ is the slope taken from the MC at time t divided by maximum MC ($MC_t/MC_{max} < 0.6$) vs the square root of time relation (Yu et al 2008).

Thickness swelling rate was further analyzed using the following equation (Shi and Gardner 2006)

$$TS(t) = \left(\frac{T_\infty}{T_0 + (T_\infty - T_0)e^{-Ksrt}} - 1\right) \times 100 \quad (8)$$

where $TS(t)$ is the thickness swelling at time t, T_0 and T_∞ are the initial and equilibrium sample thickness, respectively, and K_{sr} is an initial (or intrinsic) relative swelling rate.

Fungal Decay

The fungal decay durability of the WPCs was evaluated using AWPA E10-06 (AWPA 2007) with a modification of the sample size and placement. Two fungi were used: a white-rot, *Trametes versicolor,* and a brown-rot, *Postia placenta*. The fungi were first grown on malt extract agar. Plugs of agar covered with mycelium were placed in sterilized soil bottles touching the feeder strips. *P. placenta* was inoculated on pine feeder strips; *T. versicolor* was inoculated on yellow-poplar feeder strips. The soil bottles were incubated for 2 wk at 28°C until the feeder strips were covered by mycelium.

The injection-molded tensile specimens were machined to 25.0 × 21.0 × 2.5 mm. A total of 12 samples per treatment (6 per fungus type) were prepared. Sets of ten randomly selected cubes (12 mm) cut from southern pine sapwood and yellow-poplar were used as controls to ensure sufficient fungal activity in the test. The surfaces of the WPC samples were sanded with 100-grit sandpaper to expose wood fibers. All the samples were oven-dried at 105°C for 24 h and weighed to the nearest 0.001 g. The WPC samples were soaked in water at room temperature for 1 wk and then under vacuum for 2 h. WPC and wood block (control) samples were wrapped with aluminum foil and sterilized in an autoclave at 121°C for 45 min. Decay chambers were prepared in 450 mL glass jars filled with 250 g of potting soil and 80 g of water with either southern pine or yellow-poplar feeder strips on top of the soil. The prepared jars were steam-sterilized in an autoclave for 45 min at 121°C.

Three sterilized samples were placed in each soil bottle. The WPC samples were inserted halfway (lengthwise) into the soil adjacent to the feeder strip. The soil bottles were incubated at 28°C. After 17-wk exposure, the samples were removed, brushed to remove mycelium, dried 24 h at 105°C, and weighed for MC measurement. The percentage mass loss (on a dry-wood basis) from fungal decay was calculated.

Table 1. *Average mass loss (standard deviation), bulk density, and moisture sorption characteristics of wood flours on extraction.*[a]

Species	Mass loss on extraction (%)	Bulk density (kg/m^3)		MC_{max} (%) 20°C, 95% RH		Diffusion coefficient (10^{-10}m^2/s)	
		Unextracted	Extracted	Unextracted	Extracted	Unextracted	Extracted
Osage orange	21.2 (0.2)	341 (22)	282 (19)	14.3 (0.60)	20.3 (0.45)	1.24 (0.03)	1.92 (0.07)
Redcedar	7.4 (0.3)	243 (24)	159 (10)	18.8 (0.02)	20.0 (0.57)	1.84 (0.03)	5.40 (0.02)
Cherry	9.0 (0.2)	249 (21)	188 (22)	17.8 (0.44)	20.7 (0.37)	2.34 (0.10)	4.07 (0.05)
Pine	8.2 (0.2)	258 (19)	163 (11)	19.1 (0.16)	20.8 (0.43)	2.76 (0.05)	5.63 (0.50)

[a] Three replicates were made for each measurement except diffusion coefficient, which was duplicated.

RESULTS AND DISCUSSION

Extraction

The mass losses after extraction were 7.4, 8.2, and 9.0% for redcedar, pine, and cherry, respectively (Table 1). Although the amount of extractives varies among wood species, within wood (sapwood and heartwood), solvent systems used, and extraction methods, it generally ranges from 2 – 10% of the dry mass of wood with some wood species containing as much as 20 – 25% extractives (Koch 1972; Fengel and Wegener 1984; Mantanis et al 1994; Taylor et al 2002). The mass loss of the Osage orange wood flour was 24.4%, which is consistent with values reported in the literature (Wang and Hart 1983). Extracted wood flours had lower bulk density than the unextracted ones (Table 1).

The natural resistance of wood, including the wood species used in this study, is in large part from the types of extractives present as well as the absolute amounts. However, the effect of individual extractive fractions on fungal resistance is not clear and relatively few individual compounds have been isolated and tested (Taylor et al 2002). The resistance of eastern redcedar (*Juniperus virginiana*) to termites has been attributed to the sesquiterpene alcohols, cedrol, and widdrol (McDaniel et al 1989). Cedrol (from *Taiwania cryptomerioides*) was also shown to have antifungal properties (Chang et al 2003). In the case of Osage orange (*Maclura pomifera*), tetra- and pentahydroxystilbenes are known to inhibit fungal growth (Barnes and Gerber 1955; Wang et al 1976; Wang and Hart 1983.

In future work, it would be useful to analyze the extracts from the wood species used in this study. Such information could help to explain the variations in properties of WPCs made with (extracted and unextracted) wood of various species.

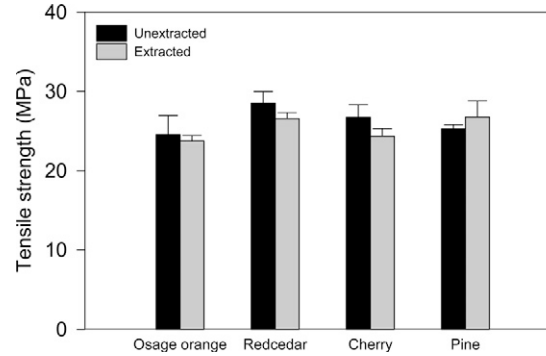

Figure 1. Tensile strength of extracted and unextracted wood–plastic composites.

Tensile Testing

The tensile strength and modulus data for the WPCs are shown in Figs 1 and 2. The one-way analysis of variance (ANOVA) followed by Tukey's multiple comparison tests of the effect of wood species on various properties are shown in Table 2. Two-sample t-test results for each species are shown in Table 3. The tensile strength of WPC samples prepared with extracted wood flours was lower on average than for unextracted wood flour WPCs, except for the pine WPCs. For unextracted wood WPCs, the tensile strength of redcedar WPC was higher than those of WPCs made with Osage orange and pine ($p < 0.05$, from one-way ANOVA followed by Tukey's multiple comparison test; Table 2). Differences in mechanical properties of WPCs from species were reported previously (Kim et al 2009). For

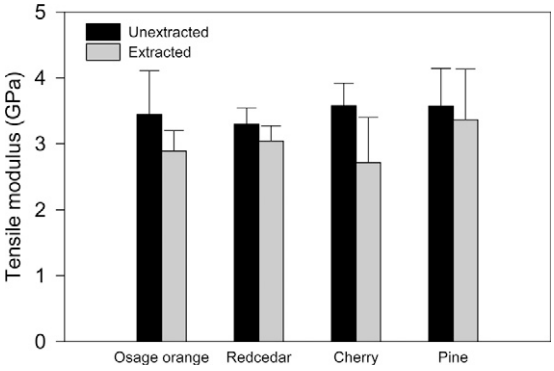

Figure 2. Tensile modulus of extracted and unextracted wood–plastic composites.

extracted WPCs, the tensile strength of redcedar and pine WPCs was higher than that of Osage orange WPCs (Table 2).

The tensile modulus of extracted flour WPCs also tended to be lower than for WPCs made with unextracted wood (Fig 2). There were no statistically significant differences among species within each composite type (Table 2). Our observation of lower mechanical properties of WPCs with extracted flour is in contrast to what Saputra et al (2004) found in their study with compression-molded WPC samples using extracted pine and Douglas-fir wood flour (40 wt%) and PP (60 wt%). They claimed that such extraction improved mechanical properties because of an improvement in interfacial shear strength between the PP matrix and the extracted wood filler.

The decrease in mechanical properties after extraction that we observed could be from the increase in the hydrophilicity of extracted wood surfaces. This could be caused by migration of nonpolar extractives toward wood surfaces and a subsequent increase in the wettability of the surface after extraction with organic solvents or heat treatment (Maldas and Kamdem 1999; Nussbaum and Sterley 2002; Nzokou and Kamdem 2004). However, more complete extraction with ethanol and boiling water may remove more polar extractives and further increase hydrophilicity of wood surfaces (Maldas and Kamdem 1999), thus deteriorating the interfacial

Table 2. *Effect of wood species on various properties of wood–plastic composites made with extracted or unextracted wood flours.*[a]

Species	Tensile strength		Tensile modulus		MC_{max}		Diffusion coefficient		TS_{max}		Thickness swelling rate		Mass loss from brown rot		Mass loss from white rot	
	Unextracted	Extracted	Unextracted	Extracted	Unextracted	Extracted	Unextracted	Extracted	Unextracted	Extracted	Unextracted	Extracted	Unextracted	Extracted	Unextracted	Extracted
Osage orange	B	C	A	A	A	A	C	BC	B	BC	C	B	B	B	B	B
Redcedar	A	AB	A	A	A	A	C	C	B	C	C	B	B	B	B	B
Cherry	AB	BC	A	A	A	A	B	AB	A	AB	B	AB	B	A	B	A
Pine	B	A	A	A	A	A	A	A	A	A	A	A	A	A	A	B

[a] One-way analysis of variance followed by Tukey's multiple comparison test results. Different letters within a column indicate a statistically significant difference ($p < 0.05$) among wood–plastic composite types. (The highest values from each test were assigned as A and the lowest as C.)

Table 3. *Effect of extraction on various properties of wood–plastic composites (WPCs).*[a]

Species	Tensile strength		Tensile modulus		MC_{max}		Diffusion coefficient		TS_{max}		Thickness swelling rate		Mass loss from brown rot		Mass loss from white rot	
	Unextracted	Extracted	Unextracted	Extracted	Unextracted	Extracted	Unextracted	Extracted	Unextracted	Extracted	Unextracted	Extracted	Unextracted	Extracted	Unextracted	Extracted
Osage orange	N		N		N		Y		Y		Y		Y		Y	
Redcedar	Y		N		N		Y		Y		Y		Y		Y	
Cherry	Y		Y		N		N		Y		N		Y		Y	
Pine	N		N		N		Y		Y		Y		N		Y	

[a] Two sample t-test results. Y: significant difference ($p < 0.05$) between unextracted and extracted WPCs. N: no significant difference ($p > 0.05$) between unextracted and extracted WPCs.

bond strength with the hydrophobic PP matrix. WPCs made with extracted wood flours also possess more wood material than those made with unextracted wood because the bulk density of extracted wood flours was reduced. Because the WPC samples were manufactured based on the mass of wood, increased wood material in WPCs with extracted wood flours could affect mechanical properties.

Other possible explanations for the differences in extraction effects observed in this and previous studies are the differences in the solvent systems used and differences in the sample preparation process (injection vs compression molding). Further studies are necessary to more fully explore the effect of extractive removal on the mechanical properties of WPCs.

Water Sorption and Thickness Swelling

Water uptake data of the WPC samples made with extracted and unextracted wood flour are shown in Fig 3. In general, extracted flour WPC samples sorbed water faster than those made with unextracted wood, except for the pine WPCs. For unextracted wood WPC samples, Osage orange and redcedar WPCs sorbed water more slowly than cherry and pine WPCs. Furthermore, extracted flour Osage orange and cedar WPCs sorbed water more slowly than extracted cherry and pine WPCs. In contrast

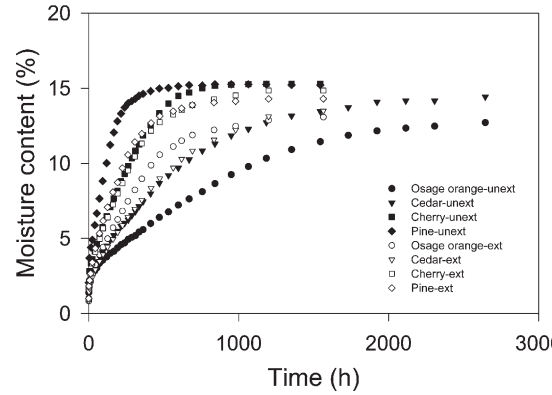

Figure 3. Water sorption of extracted and unextracted wood–plastic composites.

Table 4. *Average (standard deviation) maximum MC, diffusion coefficient, maximum thickness swelling, and thickness swelling rate of wood–plastic composite samples made with unextracted and extracted wood flours from four different species.*[a]

Species	MC_{max} (%)		Diffusion coefficient (10^{-13}m^2/s)		TS_{max} (%)		Thickness swelling rate (10^{-3}/h)	
	Unextracted	Extracted	Unextracted	Extracted	Unextracted	Extracted	Unextracted	Extracted
Osage orange	25.4 (1.8)	26.1 (0.5)	0.90 (0.08)	2.11 (0.22)	2.8 (0.4)	5.5 (0.2)	1.86 (0.41)	3.23 (0.45)
Redcedar	29.0 (2.5)	27.0 (3.5)	1.03 (0.25)	1.65 (0.56)	3.0 (0.3)	5.0 (0.5)	1.61 (0.62)	3.40 (1.45)
Cherry	30.6 (2.9)	29.7 (0.5)	2.53 (0.31)	2.56 (0.14)	3.9 (0.4)	6.2 (0.2)	4.64 (1.21)	4.81 (0.46)
Pine	30.5 (1.8)	28.6 (2.2)	4.68 (0.25)	2.81 (0.20)	4.5 (0.7)	6.3 (0.6)	9.39 (2.10)	5.26 (0.67)

[a] MC_{max} values are based on dry wood mass. Five replicates were made for each measurement.

with the other species, WPC samples made with extracted pine sorbed water more slowly than those made with unextracted pine.

The moisture sorption characteristics of wood flours and WPCs were further analyzed by Fick's law using Eqs 4 – 6 for WPCs and Eq 7 for wood flours. The diffusion coefficient (D) and other water sorption and thickness swelling data are presented in Table 1 (wood flours) and Table 4 (WPCs). The moisture sorption characteristics of WPCs appeared to be affected by the wood flour used. For example, the low diffusion coefficients of Osage orange and redcedar wood flour were associated with the low diffusion coefficients of WPCs made with the same species.

In general, extracted wood flour sorbs more moisture than unextracted flour. In addition, the bulk diffusion coefficients of extracted wood flour were higher than those of unextracted wood flour. The diffusion coefficients of extracted wood WPC samples were generally higher than for WPCs made with unextracted wood, except for the pine WPCs (Table 4).

The thickness swelling of the WPC samples showed a similar pattern to the water uptake data (Fig 4). In general, the thickness of extracted wood WPC samples increased more rapidly than samples made with unextracted wood, except for the pine WPC samples. At the end of the test, the maximum thickness swelling (TS_{max}) of extracted wood WPC samples was greater than that of samples made with unextracted wood (Tables 4 and 5). The thickness swelling rate parameter (K_{sr}) was calculated based on Eq 8 and the values for each sample are presented in Table 4. The thickness swelling rate was higher

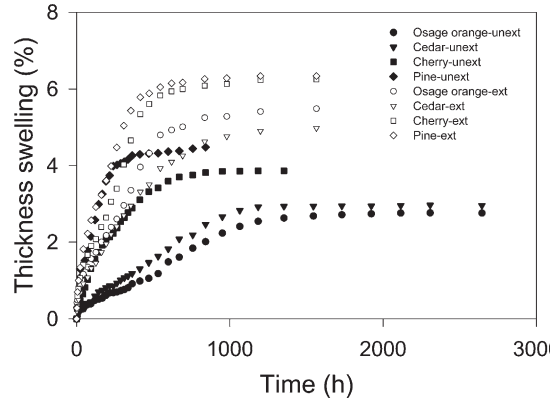

Figure 4. Thickness swelling of extracted and unextracted wood–plastic composites.

for the extracted wood samples than for the samples made with unextracted wood, except for the pine WPCs. The thickness swelling rate results followed a similar pattern as the diffusion coefficient results.

The hygroscopic properties of wood can be affected by extractives (Spalt 1957; Wangaard and Granados 1967; Skaar 1988; Choong and Achmadi 1991; Mantanis et al 1994; Maldas and Kamdem 1999; Nzokou and Kamdem 2004. Extracted wood generally sorbs more water and swells more than unextracted wood from increased availability of moisture sites previously occupied by extractives and increased diffusion coefficient (Nearn 1955; Spalt 1979; Taylor 1974). The increased water sorption and thickness swelling characteristics of extracted WPCs as well as wood flours in this study are consistent with previously results with solid wood except pine WPCs (Spalt 1957; Wangaard

Table 5. *Average MC (standard deviation) of wood–plastic composites made with extracted and unextracted wood flours after 17-wk exposure in modified soil block tests.*[a]

	Brown rot		White rot	
Species	Unextracted	Extracted	Unextracted	Extracted
Osage orange	17.9 (1.0)	25.1 (1.8)	17.8 (0.7)	26.8 (4.0)
Redcedar	16.2 (1.4)	24.3 (1.8)	16.0 (1.6)	27.6 (5.4)
Cherry	18.8 (2.1)	34.5 (5.1)	18.0 (1.5)	30.4 (1.9)
Pine	17.0 (0.6)	34.5 (1.7)	17.7 (0.9)	26.8 (5.5)

[a] Six replicates were made for each measurement.

and Granados 1967; Choong and Achmadi 1991; Mantanis et al 1994).

Interestingly, the water sorption characteristics of pine WPCs did not correspond to that of the pine wood flour. Compared with the unextracted, the diffusion coefficient of extracted pine WPCs decreased, whereas that of extracted wood flour alone increased. Such inconsistency may suggest that the water sorption characteristics of extracted pine WPCs are more influenced by the interaction between the wood flour and the matrix than by the properties of the wood flour itself.

Some species such as eastern redcedar are known to have relatively low volumetric swelling and shrinkage (Simpson and TenWolde 1999; Suchsland 2004). In addition, the swelling of the wood component in WPCs affects the composite's microstructure by expanding cracks, debonding wood–plastic interfaces, and thereby providing more pathways for water penetration (Steckel et al 2007). The low moisture sorption and thickness swelling characteristics of WPCs made with unextracted cedar and Osage orange are likely the result of the low water sorption and low volumetric swelling of the wood component.

As stated earlier, removal of extractives can increase the availability of hygroscopic sites previously blocked by extractives. This increased hydrophilic nature of extracted wood may result in an increase in thickness swelling rate for extracted wood WPC samples. In addition, from the lower bulk density of extracted wood flour, more wood is in WPCs made with extracted wood, which provides more material for water sorption and thickness swelling.

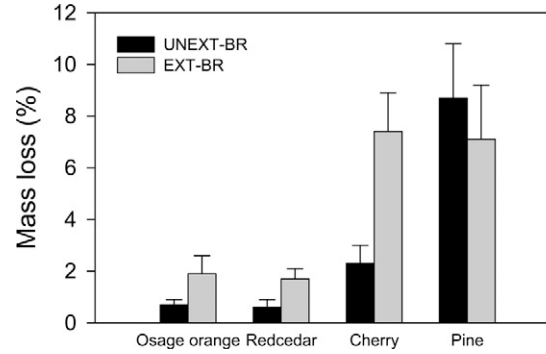

Figure 5. Mass loss of wood–plastic composites by *P. placenta* (brown rot).

Fungal Decay

The MC of unextracted wood WPCs after pretreatment and 17 wk in the moist soil of the decay tests ranged from 16 – 19%, whereas that of extracted wood WPC samples ranged from 24 – 34% (based on wood mass) (Table 5). The average mass loss of the solid wood controls was 35% for both brown rot on pine and white rot on yellow-poplar, indicating that the test conditions were sufficient for decay. The mass loss of the unextracted wood WPCs was low overall (Figs 5 and 6), ranging from about 0.6 – 8.7% for *P. placenta* (brown rot) and 0.4 – 3.2% for *T. versicolor* (white rot). Low fungal decay of WPCs made with unextracted Osage orange and redcedar could be attributable to their low moisture sorption behavior and/or to the natural durability of the wood itself (Kim et al 2008).

The mass loss of the extracted wood WPCs from fungal attack was higher than that of unextracted wood WPCs, ranging from about 1.7 – 7.4% for *P. placenta* (brown rot) and 5.5 – 24.8% for *T. versicolor* (white rot). This is in agreement with previous research with solid wood in which extractive removal increased weight loss from fungal degradation (Scheffer and Cowling 1966; Smith et al 1989). The increased mass loss of WPCs with extracted wood flour could be from the absence of extractives that protect the wood and/or increased water sorption characteristics. In addition, the higher

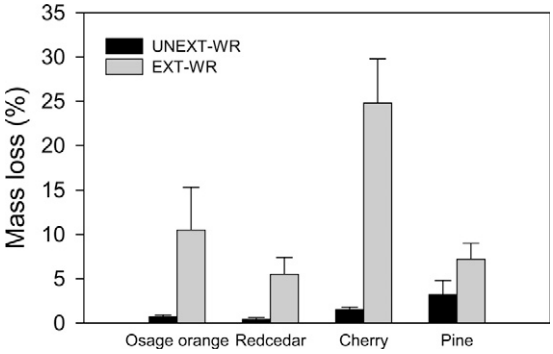

Figure 6. Mass loss of wood–plastic composites by *T. versicolor* (white rot).

wood content in the extracted WPCs could also attribute to the increased mass loss.

Interestingly, the average mass loss of extracted pine WPCs by *P. placenta* (brown rot) was slightly lower than for the samples made with unextracted pine flour. This could be from the reduced water sorption and thickness swelling characteristics. The mass loss from the white rot of the extracted pine WPCs was higher than for the unextracted pine WPCs.

The reduced water uptake, improved mechanical properties, and (in the case of brown rot) increased decay resistance of extracted pine WPCs were interesting because it was consistently in contrast to the other species. It appears that, in the case of pine, the extraction process improved interfacial bond strength, possibly through the removal of hygroscopic materials. These extractives may have included sugars and starches that could provide additional nutrition for fungal decay. The differing effects of extraction with different wood species merit further investigation.

It is also notable that the extracted wood WPCs made with the different species were not uniform in their properties. This suggests that the method used here for the preparation of "extractive-free" wood does not result in completely extractive-free wood. The different colors of the extracted wood flours that we observed support this conclusion, because color in wood is largely a function of extractives. Magel et al (1995) have noted that during heartwood formation in some species, phenolic substances generated in the wood are tightly bound to the wood cell wall. These compounds cannot be removed using normal extraction procedures and yet are they are not considered a true part of the lignin. It is also possible that differences in types and amounts of structural components (cellulose, hemicelluloses, and lignin) among the species affect the properties of WPCs.

CONCLUSIONS

The effect of wood extractives on the water sorption and durability of WPCs was studied. Extracted and unextracted flour from four wood species (two hardwoods and two softwoods) and polypropylene were used to make WPC samples. In general, removal of extractives from the wood resulted in a decrease in mechanical properties of WPCs, an increase in diffusion coefficient, and maximum thickness swelling and thickness swelling rates with the exception of WPCs made with pine. These trends in mechanical properties and water relations could be from the increased hydrophilicity of the wood surface and the decreased bulk density of the wood on extraction.

WPCs made with extracted wood flour tended to have lower fungal durability than unextracted wood WPCs. The removal of fungal-inhibiting extractives, especially in eastern redcedar and Osage orange, combined with increased moisture sorption rates and resulting thickness swell may explain the decrease in fungal durability.

ACKNOWLEDGMENT

This research was supported by the Wood Education and Resource Center (Award No. 06-DG-219).

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