INFLUENCE OF HEMICELLULOSE EXTRACTION ON WATER UPTAKE BEHAVIOR OF WOOD STRANDS

Yang Zhang
Professor
College of Wood Science and Technology
Nanjing Forestry University
Nanjing, P.R. China

Omid Hosseinaei
Postdoctoral Research Associate

*Siqun Wang**†
Associate Professor
Center for Renewable Carbon
University of Tennessee
Knoxville, TN 37996

Zhaobing Zhou
Lecturer
College of Wood Science and Technology
Nanjing Forestry University
Nanjing, P.R. China

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Abstract. Hemicellulose is the most hydrophilic and unstable of wood polymers. This study examined the effect of decreasing the amount of hemicellulose in wood on wettability and water uptake behavior of wood strands. Two methods were used for decreasing hemicellulose in wood strands: hot-water extraction and enzyme treatment. Contact angle measurements showed a decrease in wettability of wood strands after hot-water extraction of hemicellulose. These results indicated a decrease in hydrophilic character of wood strands. Amount of water taken up by strands treated with hot-water extraction decreased as percentage of mass loss increased. The enzyme-pretreated wood strands also absorbed water at lower rates compared with untreated samples. Results indicated that hemicellulose has a great influence on water absorption of wood and that decreasing hygroscopocity of wood by extraction of hemicelluloses is possible.

Keywords: Water uptake, wettability, hemicelluloses, hot-water extraction, enzyme treatment.

INTRODUCTION

The main components of wood are cellulose, hemicellulose, and lignin, which are natural polymers containing hydroxyl groups that readily form hydrogen bonds with water, thus causing a high rate of water uptake and consequently dimensional instability in both wood and wood-based materials. Wood deforms as it adsorbs or desorbs water because it is a hygroscopic biological material with a porous structure (Inagaki et al 2008). Water absorption can also release internal stress in wood-based composites, causing thickness swelling and dimension instability (Wang and Winistorfer 2001). Hawke et al (1993) found a close relationship between mat moisture content of wood composites and their thickness swell, water absorption, and linear expansion. Linear relationships have been found between thickness swelling of flakeboard and its relative moisture absorbed (Lu and Lam 2001).

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* Corresponding author: swang@utk.edu
† SWST member

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Decrease in hygroscopicity and water uptake can improve dimensional stability and performance of wood and wood-based composites.

General methods to decrease water uptake include adding some kind of waterproofing additive or resin treatment to wood and wood-based materials. Water uptake decreased as waterproofing additives, such as wax, were increased (Zhang et al 2007). It has been proven that resin level has a significant influence on thickness swell and water absorption values of flakeboard (Gardner et al 1990). In recent years, scientists have paid more attention to using heat treatments to decrease water absorption of wood (Metsa-Kortelainen et al 2006). The main effect heat treatment has on wood is to decrease free hydroxyl groups in the holocellulose because of degradation of hemicelluloses, the most reactive, unstable, and hydrophobic wood component (Tjeerdsma and Militz 2005). With this treatment, water repellence of wood can be improved and its dimensional stability can be increased (Kocaefe et al 2008). Kocaefe et al (2008) showed that the increase of surface contact angle between heat-treated wood and water was much greater in the axial direction than in the radial and tangential directions. The hydrophobic character of wood may also be increased by oil-heat treatment (Petric et al 2007). It also has been proven that panels made of heat-treated fiber have a less hydrophilic character (Garcia et al 2008).

Another new way to decrease hygroscopicity is to extract hemicellulose from wood strands before making panels. It has been shown that extraction of hemicellulose decreases the number of hydroxyl groups and consequently the hygroscopicity of wood. Extraction of hemicellulose improved dimensional stability, decreased water absorption, and improved mold resistance of flakeboard panels (Hosseinaei et al 2011a). Also, this method provides sugars for making biofuel, a renewable source for energy production.

As previously stated, all wood macromolecules have the capacity to adsorb water and decreasing adsorptive capacity of wood increases its dimensional stability. However, until now, the relative contributions of the different components of wood in the sorption process have not been clearly shown (Barrera-Garcia et al 2008). The main objective of this article was to investigate the influence of hemicellulose extraction from wood on its wettability and water uptake behavior and to explain its function during adsorption of water.

MATERIALS AND METHODS

Materials

Southern Yellow Pine (*Pinus* spp.) was obtained from J.M. Huber Corporation (Knoxville, TN). Logs were debarked and shipped to Louisiana-Pacific Co. R&D Technology Center (Franklin, TN) for flaking. Average length of prepared strands was 150 mm with a thickness of approximately 0.8 mm and random width. Fresh-cut strands were directly shipped to North Carolina State University (Raleigh, NC) for hot-water extraction.

Concurrently, poplar (*Populus euramevicana*), from Jiangsu province in China was also debarked and processed into strands. The strands were about 120 mm long, 20 mm wide, and 1.2 mm thick. Fresh-cut strands were used for enzyme treatment at Nanjing Forestry University, China.

Hemicellulose Extraction

Extraction of hemicellulose was performed by a batch reactor with a total capacity of 70 L using hot water. Treatment was performed for two durations (30 and 60 min) and at three temperatures (140, 155, and 160°C) with two repetitions for each condition. Each time, 5 kg of strands with approximately 70% MC was loaded into the reactor at a water:solid ratio of 20:1 by weight. For exact measurement of mass loss of strands caused by extraction, samples from 50-g oven-dried strands (MC = 0%) were prepared and placed separately in a bandage cloth between other strands in the reactor. Mass loss of the sample caused by extraction was calculated according to the following formula:

$$ML = \frac{m_0 - m_1}{m_0} \times 100 \tag{1}$$

where ML = percentage of mass loss, m_0 = initial oven-dried weight of sample before extraction, and m_1 = oven-dried weight of same sample after extraction.

Enzyme Treatment

Xylanase was the enzyme used for hemicellulose extraction (Imperial Jade BioTechnology Co., Ltd., China). Lemon acid and Na_2PO_4 were used as mollifying liquid (Guangdong, China). Poplar strands with liquid hemicellulase and mollifying liquid (pH 4.8) were placed in a reaction vessel and kept at 50°C. Strands were treated by hemicellulase under the following conditions: 400 U/g wood and 8-24 h duration.

Sample Preparation

Wood strand samples of Southern Yellow Pine and poplar were cut into specimens of $10 \times 10 \times 0.8$-1.2 mm. To control influence of the samples' moisture content on results, all prepared specimens were placed into desiccators above a saturated water solution of potassium acetate that maintained 23% RH at room temperature of 21-23°C. Final moisture content of specimens was about 5%.

Contact Angle and Surface Free Energy Measurement

Contact angle measurement was performed at room temperature with the sessile drop method. A JC2000A contact angle meter (Shanghai Zhongchen Digital Technology and Equipment Co., Shanghai, China) was used to measure drop changes and automatically record contact angle during contact time. Surface free energy was calculated from contact angle of diiodomethane, glycerol, and distilled water, whereas surface free energy values of different samples were calculated by the plot extrapolation method. Contact angle and surface free energy measurements were performed only for hot-water-extracted samples.

Water Uptake Measurement

The Wilhelmy plate method was used to evaluate wicking behaviors of wood (Zhang et al 2007). The test was performed with a Cahn DCA-322 dynamic contact analyzer (DCA 322; Thermo Cahn Instruments, Madison, WI). With the DCA 322 technique, the sample is supposed to be immersed and held just below the liquid surface; weight change (amount of water absorbed by the sample) is recorded as a function of time. In this study, the sample was immersed 1.0 mm into the distilled water, and it was held in this fixed position by the electrobalance attached to the instrument. The sample was held with its grain parallel (referred to as parallel-to-grain) to the immersion direction. Weight change was recorded as a function of time. Total run time for each specimen was 8 h (28,800 s), and data were collected at various intervals. The test was performed at room temperature (21-23°C).

RESULTS AND DISCUSSION

Contact Angle and Surface Free Energy of Hot-Water-Extracted Samples

Figure 1 shows contact angle change of water as a function of wood strand extraction, which reflects the influence of hemicellulose extraction on the water uptake process, especially at the early stage. Different mass losses (0, 6.8, 9.5, 14.1, 20.0, and 26.8%) are related to the control sample and extraction conditions of 140°C at 30 min, 155°C at 30 min, 155°C at 60 min, 170°C at 30 min, and 170°C at 60 min, respectively. Smaller contact angle showed better wettability and more water absorption by wood strands. Increase in contact angle after hot-water treatment indicates a change in the naturally hydrophilic character of wood to a more hydrophobic character. Removing hemicellulose can decrease the number of hydroxyl

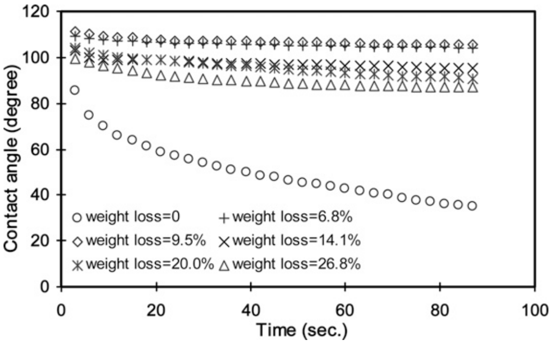

Figure 1. Contact angle of water for hot-water-extracted strands (pine) as a function of time.

groups and make wood less hydrophilic. Also, it is possible that the proportion of lignin or other less hydrophilic components on the strand surface increases after hot-water treatment (Hosseinaei et al 2011b). It was found that contact angle decreased with increasing contact time (Fig 1). Water penetration into the porous structure of wood (including lumens and pores in cell wall) may be the reason for the decrease in contact angle during contact time. Contact angle of treated and untreated samples decreased during contact time, indicating the penetration of water into the porous structure of wood strands. Also in extracted samples, those with greatest weight loss (26.8%) had lower contact angles compared with other extracted samples. These samples had the greatest hemicellulose extraction and were expected to show greater hydrophobicity, but probably because more or larger pores were created during extraction, these samples had the greatest water penetration into the porous structure and the lowest contact angle. Paredes et al (2009) reported that the severe condition of hot-water extraction will result in micropore formation and increased pore volume in cell walls. However, there was only a small change of contact angle during contact time for strands treated by hemicellulose extraction. For example, contact angle only decreased from 111.2-105.5° during contact with water (3-87 s) for treated samples (9.5% weight loss). In contrast, contact angle change for untreated strands was greater, from 85.4-35.3° during contact with water (3-87 s).

Table 1. Surface free energy of hot-water-extracted samples (pine).

Mass loss (%)	Surface free energy (mJ/m^2)[a]
0	41.3 (7.8)
6.8	26.1 (6.1)
9.5	21.4 (3.8)
14.1	23.7 (6.5)
20.0	22.3 (6.3)
26.8	25.1 (4.6)

[a] Standard deviation shown in parentheses.

Pétrissans et al (2003) reported that heat treatment decreases wettability of wood as well as increasing its hydrophobicity.

Results for surface free energy of samples are given in Table 1 and show that total surface free energy significantly decreased after hot-water treatment. Results after thermal treatment of wood (which also caused hemicellulose degradation) have shown a decrease in the polar component of surface free energy (Gérardin et al 2007). A decrease in surface free energy of wood strands shows that the strand surface becomes less polar after extraction, resulting in lower wettability. Surface free energy of all extracted samples was almost in the same range.

Influence of Hot-Water Hemicellulose Extraction on Water Uptake

Walinder and Gardner (1999) showed that wicking is a process by which liquid may penetrate spontaneously into wood by capillary force. Water uptake behavior of wood-based composites is closely connected with properties of wood itself because thickness swelling and linear expansion are associated with the amount of water absorbed by wood. In tests, it has been found that the general shape of water uptake curves for wood strands (Figs 2 and 3) was similar to that of veneer and other natural fibers (Esperta et al 2004; Son and Gardner 2004). The water uptake process includes two stages: a rapid absorption and a longer, slower, relatively linear absorption. In our test, strands clearly absorbed more water, and faster, at the early stage of the water uptake test compared

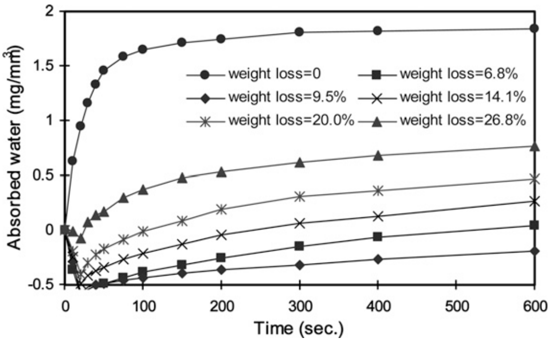

Figure 2. Water absorption of hot-water-extracted strands (pine) in the first stage.

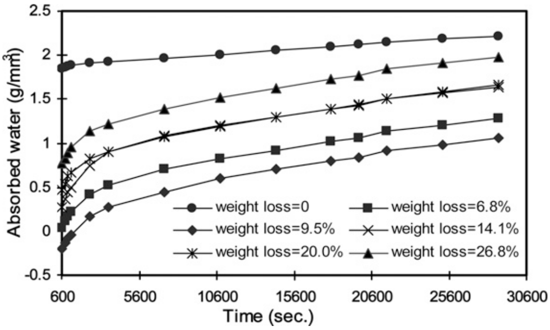

Figure 3. Water absorption of hot-water-extracted strands (pine) in the second stage.

with the second, later stage (Figs 2 and 3). The first stage was defined as lasting until 10 min after beginning the test, and the rest of the test period was called the second stage.

In Figs 2 and 3, weight loss indicates removal of hemicellulase because weight loss of the wood sample was mainly caused by extraction of hemicellulose. Other components that possibly can be extracted during hot-water treatment are lignin and hot-water soluble extractives. Results for similar extraction methods and the same species have shown that only small amounts of lignin, up to 1.25% of total initial lignin content for extraction at 160°C and 60 min, can be extracted during this treatment (Sattler et al 2008). Hot-water soluble extractives for this species were 3.86% of dry mass of wood, and about 40% of hot-water soluble extractives (1.5% of dry mass of wood) were extracted during treatment (in all conditions, it was almost the same). From these two figures, it was found that water uptake of wood strands decreased sharply as percentage of weight loss increased from 0-9.5%. The main reason for this rapid decline was that in interactions between wood and water, the physicochemical condition of hydroxyl groups plays a key role in the water adsorption process of wood. The decrease of hemicellulose content results in a decrease of hydroxyl groups, including free hydroxyl groups, thus decreasing the water absorption capacity of wood. Although water uptake of specimens increased a little and gradually as percentage of weight loss increased from 9.5-26.8%, water absorption of untreated wood was the greatest. The greater water uptake of samples with greater weight loss may have occurred because of the possible presence of larger and more pores in these samples (as seen in contact angle results), which will increase capillary motion of water. When the wicking test reached 28,800 s (8 h), water absorption of the strand with weight loss of 26.8% reached 1.98 mg/mm^3. In the wicking test for the untreated wood strand at the same duration, water absorption was 2.21 mg/mm^3. This situation also could be explained by changes in contact angle and surface free energy in wood strands (Fig 1; Table 1). It can be deduced that samples with less water uptake have lower surface free energy and greater contact angle.

Influence of Enzyme Treatment on Water Uptake

Figures 4 and 5 show water absorption changes of poplar strands treated with enzyme in a two-stage process. Except for the initial part of the first stage, water uptake of strands treated by enzyme was less than that of untreated strands. When the wicking test reached 28,800 s (8 h), enzyme-pretreated samples had significantly lower absorbed water compared with untreated samples. Water absorption of the poplar strand that was treated for 12 h by enzyme was smallest at the end of the test. It has been proven that free hydroxyl groups of wood carbohydrates play an important role in the process of water adsorption

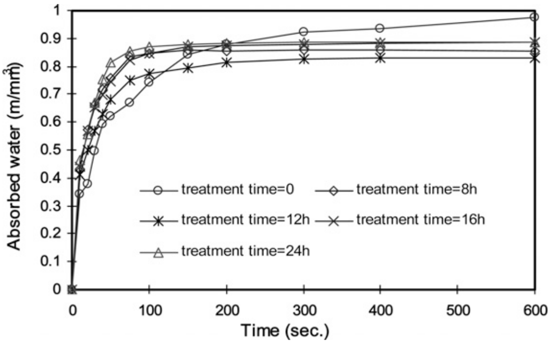

Figure 4. Water absorption of enzyme-treated strands (poplar) in the first stage.

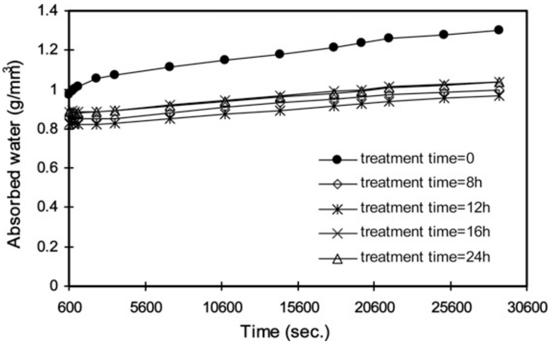

Figure 5. Water absorption of enzyme-treated strands (poplar) in the second stage.

(Boonstra and Tjeerdsma 2006). The main reason is that in untreated strands, the polyhydroxyl structure of hemicellulose provides numerous opportunities for hydrogen bonding with water molecules. These opportunities were decreased because of the way enzyme treatment converts hemicellulose into monosugars through enzymatic hydrolysis and extracts them from wood strands (Zhang et al 2009). Although xylans in plants are closely associated with cellulose and lignin, practical substrates for hydrolysis and subsequent fermentation, in most cases, would be soluble oligomers (Poutanen et al 1986). The properties of xylans are determined by the origin of the carbohydrate but also to a great extent by method of fractionation. About 60-70% of xylose residues are esterified at the hydroxyl groups of either carbon 2 or 3 or in both of these positions (Plus et al 1991).

CONCLUSIONS

This study investigated if wicking behavior of hemicellulose-extracted wood strands changed during adsorption of water. Hot-water extraction of hemicellulose resulted in decreased wettability and water uptake of wood strands. Enzyme-pretreated wood strands also absorbed less water compared with untreated strands. Results indicated that hemicellulose had a great influence on water absorption of wood and that it was possible to decrease water absorption of wood by extracting hemicellulose. Changing the character of wood from hydrophilic to more hydrophobic by hemicellulose extraction can also potentially improve dimensional stability and resistance to fungi in wood and wood-based composites.

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