Influence of Heat Treatment on the Water Uptake Behavior of Wood

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Dimensional stability is an important property of wood that is strongly influenced by its water uptake behavior. Heat treatment is one method to improve wood dimensional stability. This study investigated the effects of heat treatment on the water uptake behavior of wood using a wicking test. The thickness of the tested wood sample was similar to that of the surface wood panel in a 3-layer composite floorboard. It was treated at different temperatures ranging from 200 °C to 400 °C under a nitrogen atmosphere for 10 min to provide the test data to investigate the basic theory relating to dimensional stability of heat-treated wood processed at higher temperatures for a short length of time. During the test, the water uptake of larch (*Larix gmelinii*) and red oak (*Quercus rubra*) were recorded continuously. The heat-treated wood had a much lower water uptake ability than untreated wood during the early stage of the wicking test; untreated wood exhibited higher total water uptake. Compared with the untreated sample, the red oak wood treated at 400 °C had an average water uptake rate that decreased from 0.28 mg/mm^3 per hour to 0.038 mg/mm^3 per hour.

Keywords: Heat treated temperature; Water uptake behavior; Oxygen/Carbon ratio; Weight loss

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INTRODUCTION

In recent years, many scientists have sought economical means to utilize wood, which is an abundant renewable supply of biomass, for advanced materials, fuels, chemicals, energy, and other applications. Heat treatment can be used to improve wood's properties. In China, heat-treated wood is called "carbonized wood," and it is widely used for construction, outdoor furniture, and other applications. During heat treatment, there is a density change in the structure of wood as the temperature increases in an inert gas atmosphere (Vafaeenezhad *et al.* 2013). The layered structures of the cell walls in the wood fibers and parenchyma cells are retained below 300 °C, but they change to amorphous-like structures without the layering above 350 °C, as observed with scanning electron microscopy (SEM) (Kwon *et al.* 2009). Cellulose is one of the three main polymers in woody material; the linear polymeric structure of cellulose undergoes great changes in its chemistry, crystallinity, and microstructure during carbonization (Dumanlı and Windle 2012). Without using chemicals, heat treatment at a high temperature reduces the hygroscopicity of wood, while also improving its dimensional stability and its resistance to biological degradation (Oumarou *et al.* 2014). Based on observing the pyrolysis of nine wood samples, there are only small changes in the nanostructure of the cellulose microfibrils in the bulk wood sample treated below 250 °C. The structure of the cellulose fibrils is completely degraded in the bulk wood samples between 250 °C and 315 °C, and nanometer-sized inhomogeneities develop in pyrolyzed wood samples above a temperature of 315 °C (Smith *et al.* 2012). Heat treatment increases the contact angles and decreases the water uptake of wood. Also, wicking is reduced by approximately 70% to 80% when wood fibers are treated at 150 °C or 180 °C for 15 min, 30 min, or 60 min (Garcia *et al*. 2008). Below 300 °C, the amorphous hemicellulose and cellulose regions are degraded, and the crystallinity of the torrefied biomass increases (Chang *et al*. 2012). The char that formed at 300 °C is primarily composed of lignin and cellulose residues, and the carbohydrates are completely lost in the char produced at 350 °C. Most of the lignocellulosic features, which consist predominantly of aromatic structures, are lost at 400 °C (Cao *et al*. 2012). The lignin content decreases, and both the degree of lignin oxidation and the amount of highly condensed black carbon moieties increase with increasing temperature during biomass transformation (Wiedner *et al*. 2013). Between 250 °C and 350 °C, more structurally complicated biochars are formed, which display relatively slow sorption rates (Chen *et al*. 2012).

Dimensional stability is an important property of wood that is strongly influenced by its water uptake behavior (Zhang *et al*. 2011, 2012). This property can be improved by heat treatment. The temperature of heat treatment is usually below 250 °C, and the duration is several hours because of the wood thickness. The treatment temperature can be higher and the duration shorter if the thickness of the wood is smaller. For example, the temperature for the treatment of dry wood strands is 740 °C, with a duration of less than one minute (Wang *et al*. 2007). It is a good idea to treat the surface wood panels of 3-layer composite floorboards at a higher temperature for a shorter time to increase its dimensional stability and to achieve higher production efficiency. This is possible because its thickness is only slightly greater than that of wood strands. The objective of this study was to investigate the effects of heat treatment on wood water uptake behavior using a wicking test and also to support a basic theory for investigating changes in dimensional stability of wood that has been heat-treated at a higher temperature and for a short time.

EXPERIMENTAL

Materials

Sample preparation

Two different wood species were used, larch (*Larix gmelinii*) as a representative softwood and red oak (*Quercus rubra*) as a hardwood. The larch (*L. gmelinii*) came from the Heilongjiang Province of China, and the red oak came from the State of Tennessee in the United States. Each sample was taken from the 35th growth ring and was cut to dimensions of 30 mm (longitudinal) by 10 mm (radial) by 5 mm (tangential) with a saw. The wood sample thickness is similar to that of the surface wood panel in a 3-layer composite floorboard. The samples were dried at 105 °C for 2 h and then heated in a nitrogen atmosphere in a tube furnace, and the ambient temperature of wood samples in the furnace were set at 200 °C, 250 °C, 300 °C, 350 °C, and 400 °C. After putting the samples in the furnace, the temperature was increased at a rate of 10 °C /min, and the holding time was 10 min when the set temperature was reached. After heat treatment, all samples were kept in a desiccator before water soaking experiments.

Methods

The evaluation of the wicking behavior of wood was performed by the Wilhelmy plate method (Wang *et al*. 2007) using a Cahn DCA-322 Dynamic Contact Analyzer (DCA 322, Thermo Cahn Instruments, Madison, WI, USA). In the DCA322 technique, the sample is immersed and held just below the liquid surface, and the weight change (the amount of water absorbed by the sample) is recorded as a function of time. In this study, the immersion depth of the sample into the distilled water was 1.0 mm, and it was held in this fixed position by an electro-balance attached to the instrument. The sample was held with its grain parallel (referred to as parallel-to-grain) to the immersion direction, and the weight change was recorded as a function of time. The total running time for each specimen was 8 h (28,800 s), and data were collected at various time intervals. The test was performed at a room temperature of 21 °C to 23 °C.

The Oxygen/Carbon ratios (O/C) of samples were determined by SEM with energy dispersive spectroscopy (EDS). The EDS was used to detect oxygen and carbon of the selected location of the samples in SEM images. The SEM instrument was a JSM-7600F (JEOL Ltd., Tokyo, Japan) and the acceleration was set at 10 kV. The EDS analysis was performed by using X-act (Oxford Instruments, Oxfordshire, UK). The thermal stability was determined using thermal gravimetric analyzers (TGA; Perkin–Elmer 7 series; and Perkin–Elmer Cetus Instruments, Norwalk, CT). The temperature was set from 25 to different temperatures at a heating rate of 20 °C/min in a nitrogen atmosphere. Three tests were performed on each sample.

RESULTS AND DISCUSSION

Changes of Water Uptake for Wood Processed under Different Treatment Temperatures

During wicking, liquid penetrates spontaneously into wood by capillary force. The water uptake behavior of wood is closely connected to its properties because the thickness swelling and linear expansion are associated with the amount of water absorbed (Walinder and Gardner 1999). The test results showed that the water uptake process included two stages, a rapid uptake and a long, slow, relatively linear uptake (Figs. 1 through 4). The first stage lasted until 600 s after beginning the test, and the rest of the test period was the second stage. It was clear that the wood sample absorbed more water, and more quickly, in the early stage of the wicking test than in the second stage. For example, in the first stage, the untreated sample of larch wood absorbed 1.60 mg/mm^3 until 600 s (Fig. 1), but it absorbed only 0.48 mg/mm^3 from 600 seconds to 28,800 s (8 h) (Fig. 2). Thus, the water uptake of the wood specimens decreased step by step as the treatment temperature was increased. Although the water uptake increased slightly and gradually as the heat treatment temperature increased from 200 °C to 400 °C, the water uptake of the untreated wood was the greatest. When the wicking test reached 28,800 s (8 h), the water uptake of the red oak wood that was treated at 400 °C had only reached 0.30 mg/mm^3, having absorbed an average of 0.038 mg/mm^3 per hour. In the wicking test for the untreated red oak wood for the same duration, the water uptake was 2.24 mg/mm^3, having absorbed an average of 0.28 mg/mm^3 per hour, as shown in Fig. 4. The main reason for this difference was that the heat treatment decreased the number of hydroxyl groups (Nishimiya *et al.* 1998; Zuo *et al.* 2003), making the wood less hydrophilic. Hence, the naturally hydrophilic wood took on a more hydrophobic character.

As part of the interactions between the wood and the water, the physicochemical condition of the hydroxyl groups play a key role in water uptake. An increase in the treatment temperature decreases the number of hydroxyl groups, including free hydroxyl groups, thus decreasing the water uptake capacity of the wood. Hence, the treatment of wood by heat or carbonization improves its water repellency and dimensional stability. More structurally complicated biochars are formed at intermediate temperatures (250 °C to 350 °C), and these samples are expected to display relatively slow sorption rates in the carbonized areas. Furthermore, previous studies indicated that at approximately 300 °C, the pyrolysis of the hemicellulose and cellulose is complete, and the wood nanocomposite structure changes dramatically at approximately 300 °C (Zeriouh and Belkbir 1995; Paris *et al*. 2005). The current study also shows that for larch wood, the water uptake of the 200 °C and 250 °C heat-treated samples was almost the same, but when the sample was treated at 300 °C, the water uptake decreased remarkably. For the red oak samples, although the water uptake of the 200 °C, 250 °C, and 300 °C heat-treated samples was almost the same, when the heat treatment temperature exceeded 300 °C, the water uptake significantly decreased. It was also very clear that when the temperature was over 300 °C the samples appeared to show negative absorption of water. This was because if the heat-treated temperatures below 300 °C, wood sample absorbed water quickly, such that the weight of wood samples increased more than the buoyancy effect of the wood samples in water.

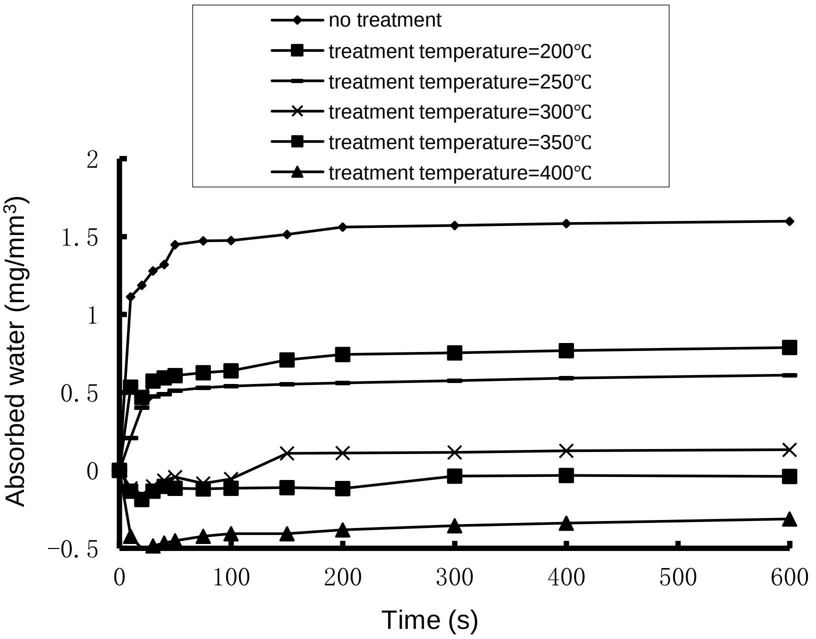

Fig. 1. Relationship between the treatment temperature and the uptake of water in the first stage for larch wood

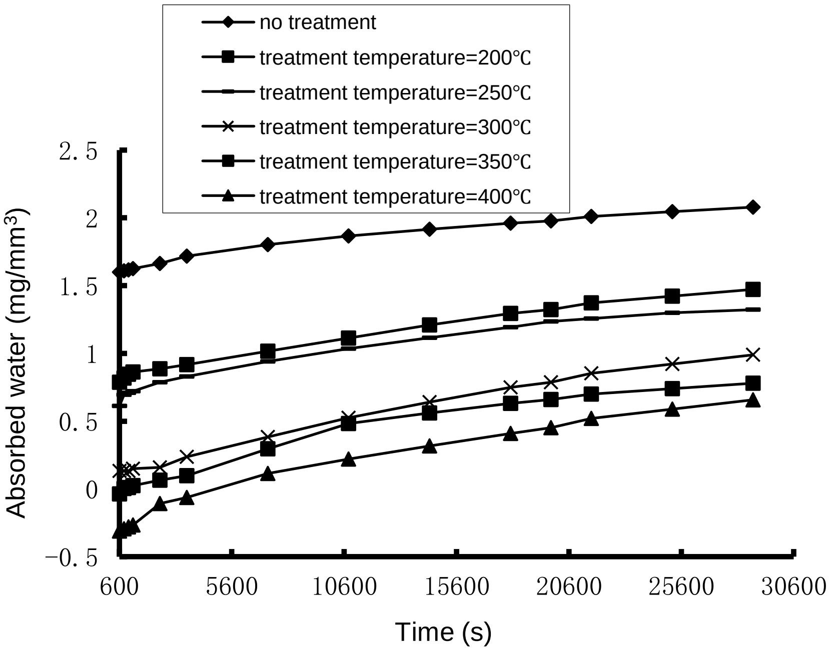

Fig. 2. Relationship between the treatment temperature and the uptake of water in the second stage for larch wood

When the temperatures were over 300 °C, hydrophobicity of wood samples increased and the material absorbed water slowly and slightly, so when immersed in water the buoyancy had a greater effect on the wood than the gravity caused by the water absorption; thus the experimental results appeared to show negative absorption. Hence, the water uptake measurement showed a transition temperature during the wood carbonization. For carbonaceous wood, the pyrolysis temperature strongly influences the thermal and chemical characteristics of the biochar samples (Azlina *et al*. 2013). The carbonaceous wood material has a better adsorption capacity in its molecular form, which depends on the electron density of the adsorbate (Lalitendu *et al*. 2013). The temperature of 400 °C is of key importance for the thermal destruction of cellulose materials (Mikova *et al*. 2013).

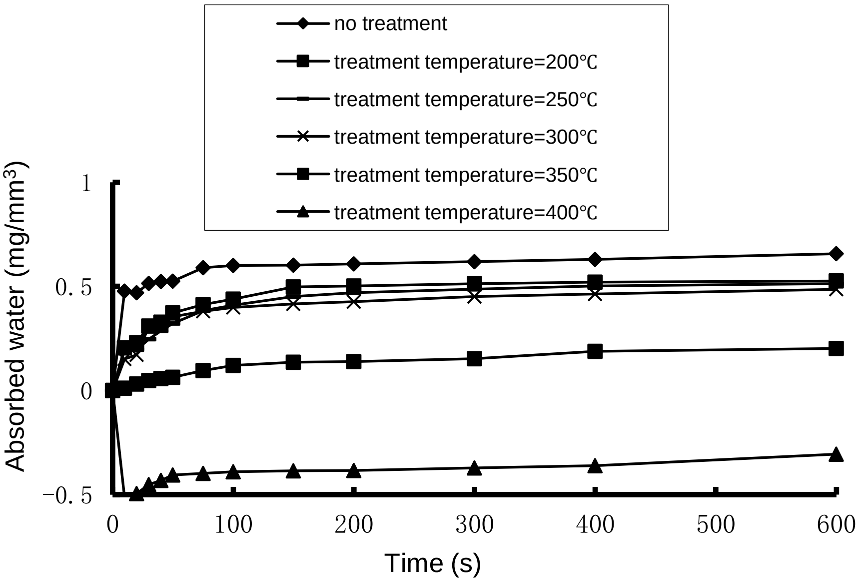

Fig. 3. Relationship between the treatment temperature and the uptake of water in the first stage for red oak wood

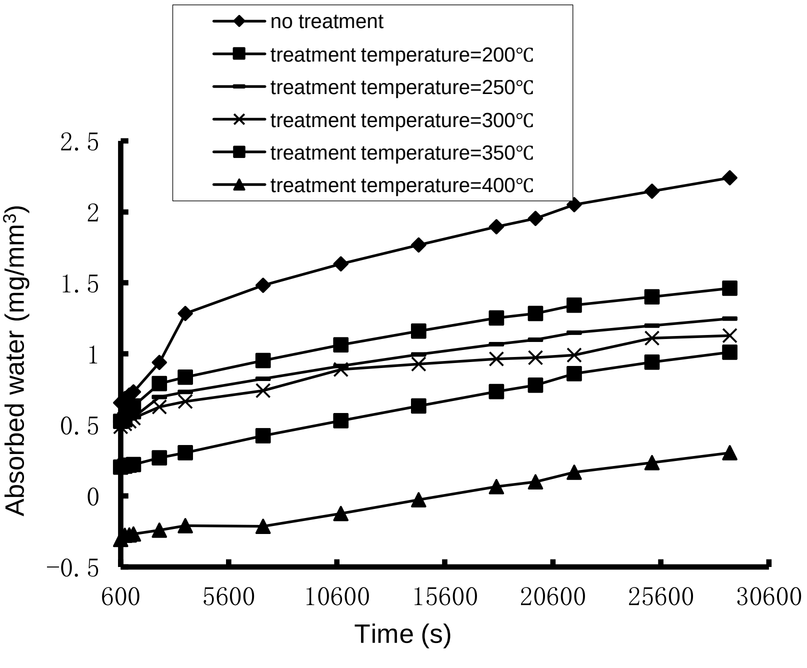

Fig. 4. Relationship between the treatment temperature and the uptake of water in the second stage for red oak wood

Change in Carbon Content of Wood under Different Treatment Temperatures

The heat or carbonization treatment was performed below 400 °C because almost all of the non-carbon atoms are removed when the wood is heated above 400 °C in an oxygen-free environment, including the oxygen and hydrogen biomass (Antal and Gronli 2003). It has been demonstrated by an X-ray photoelectron spectroscopy (XPS) analysis that the Oxygen/Carbon ratio of wood exhibits a slight decrease following such heat treatment (Garcia *et al*. 2008). In this study, SEM combined with EDS were used to evaluate the O/C ratio of wood samples, and SEM was used to determine the location for EDS detection. By the spectrum of EDS the O/C ratio of the wood samples were obtained. All O/C ratios of wood samples are shown in Fig. 5. The test results showed that the O/C ratio decreased step by step during the heat treatment from 200 °C to 400 °C. The O/C ratio of the untreated control sample was 0.89 for larch wood and 0.97 for red oak wood (Fig. 5), and the values decreased to 0.50 for larch wood and 0.26 for red oak wood after a heat treatment at 400 °C for 10 min. With respect to other related studies, although the heating rate and holding time were different, the O/C of wood changed approximatively at the same final temperature (Prins *et al*. 2006; Li *et al*. 2015). In a biomass torrefaction study, Prins *et al*. (2006) showed that compared to straw, beech and willow, the O/C ratios of larch decreased slowly with the temperature increased to 300 °C, as softwood larch has lower holocellulose and higher lignin. The different contents of softwood and hardwood caused the different elemental concentrations in pyrolysis products (Czimczik *et al*. 2002). The carbon content of the larch and red oak clearly increased with the treatment temperature. However, the change rates were different, indicating that they exhibited different water uptake behaviors.

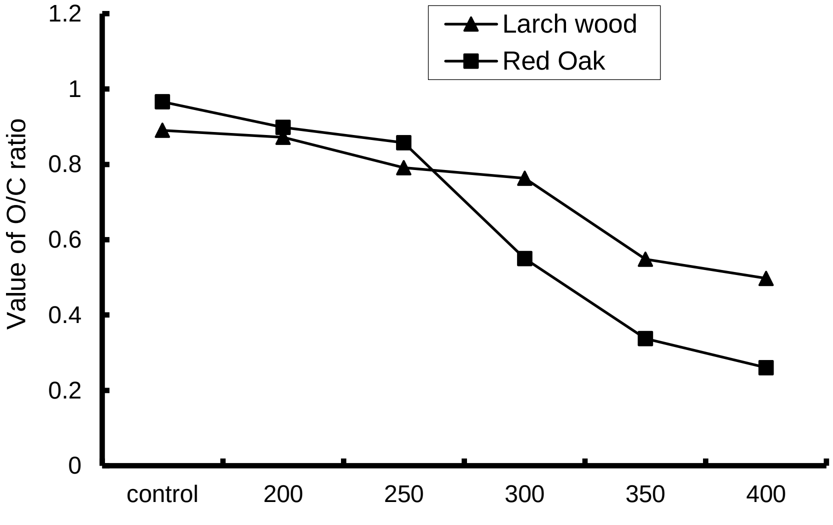

Fig. 5. Change in the O/C ratio for larch wood and red oak wood under different treatment conditions

Weight Change of Wood under Different Treatment Temperatures by Thermogravimetric Analysis (TGA)

The test results of thermogravimetric analyses are shown in Fig. 6, for the test conditions of 200 °C, 250 °C, 300 °C, 350 °C, and 400 °C for 10 min under a nitrogen atmosphere, as determined using a Perkin-Elmer 7 series instrument. The test revealed the sample weight loss percentage after a heat treatment or carbonization under a nitrogen atmosphere. The weight loss percentage for larch wood was 6.4%, 7.5%, 20.1%, 47.4%, and 70.2% and for red oak wood the weight loss percentage was 3.8%, 6.7%, 23.1%, 44.1%, and 72.8% when the heating treatment temperature was 200 °C, 250 °C, 300 °C, 350 °C, and 400 °C, respectively, for 10 min. Hemicelluloses, cellulose, and lignin decompose from 170 °C to 240 °C, 240 °C to 310 °C, and 320 °C to 400 °C, respectively (Kwon *et al*. 2009). This could change the water uptake behavior of wood because when the hemicelluloses, cellulose, and lignin decompose, the concentration of water-absorbing chemical groups decreases in different temperature ranges.

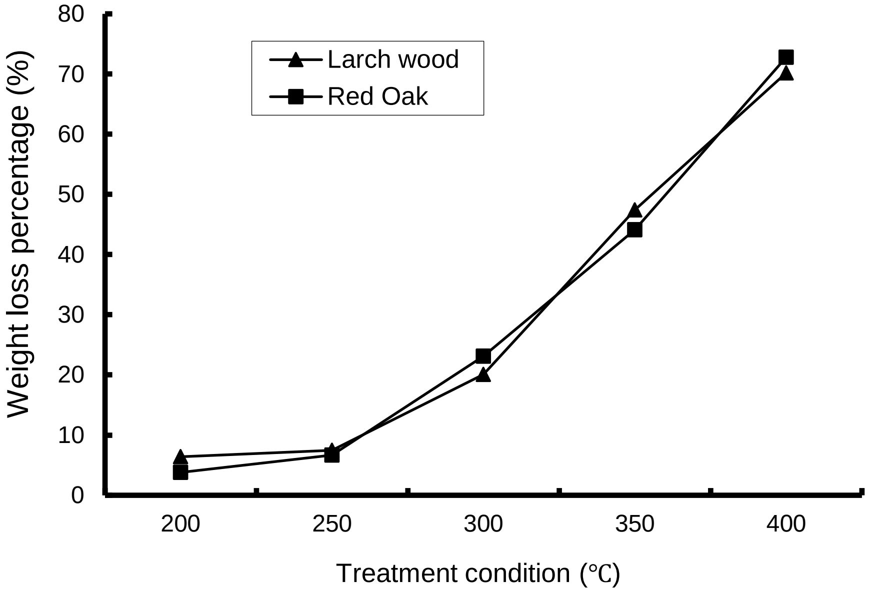

Fig. 6. Weight loss percentages of larch wood and red oak wood at different treatment temperatures under a nitrogen atmosphere

CONCLUSIONS

1. The water uptake capability of wood significantly decreased with an increase in the heat treatment temperature over a short period of time. The key temperature point was 300 °C for wood heat treatment. Over this temperature, the water uptake capability of wood decreased dramatically.
2. The decrease of water uptake capability corresponds with the weight loss and O/C ratio change. It could be concluded that the hemicelluloses, cellulose, and lignin decomposed under different temperature in the wood heat-treated process. This caused wood chemical composition to change. The water-absorbing chemical groups decreased as the heat treatment temperature increased from 200 °C to 400 °C, thus the water uptake capability of wood decreased.

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