J Wood Sci (2007) 53:454–457
DOI 10.1007/s10086-007-0877-9

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Water absorption of boron-treated and heat-modified wood

Received: September 6, 2006 / Accepted: January 5, 2007 / Published online: April, 18, 2007

Abstract Heat treatments change the chemical and physical properties of wood and dimensional stability and hygroscopicity are affected as a result of modifications of wood cell components. This study evaluated the water absorption of wood specimens treated with boron compounds followed by heat treatment. Sugi (*Cryptomeria japonica* D. Don) sapwood specimens treated with either boric acid (BA) or disodium octoborate tetrahydrate (DOT) solutions were heat-modified at either 180° or 220°C for 2 or 4 h. Carbohydrate composition and water absorption of the specimens were then measured and compared with those of untreated and unheated specimens. Wood carbohydrates were significantly degraded in the specimens after heat treatment. The heat treatment evidently decreased the water absorption and the heat-modified specimens absorbed less water than unheated specimens. The higher the treatment temperature and the longer the treatment time, the lower the amount of absorbed water. The boron-treated and heat-modified specimens, however, showed increased water absorption due to the hygroscopic properties of BA and DOT.

Key words Heat treatment · Chemical composition · Water absorption · Boron compounds

Introduction

The heat modification of wood has been widely investigated as a means to make wood a biologically durable construction material as well as to reduce equilibrium moisture content, to decrease water absorption, and to increase the dimensional stability of wood. Wood, which is originally a hydrophilic material, becomes hydrophobic after heat treatment. The heat treatment process is generally accompanied by cleavage of the lignin–polysaccharide complex of wood by organic acids released from hemicelluloses.[1–5] This change in hygroscopicity is particularly characteristic and has been attributed to chemical modifications of wood components, especially in hemicelluloses, and physical changes in wood crystallinity. The decrease in hygroscopicity has been related to a decrease in the number of hydrophilic sites in wood, especially hydroxyl groups of carbohydrates.[6] With the degrading of carbohydrates after heat treatment, the concentration of water-absorbing hydroxyl groups decreases resulting in slow water uptake and absorption. When wood is subjected to heat, acetic acid is formed from acetylated hemicelluloses by hydrolysis and this released organic acid serves as a catalyst in the hydrolysis of hemicelluloses to soluble sugars. In addition, the cellulose microfibrils in the amorphous area are depolymerized by acetic acid, which is then able to break cellulose into shorter chains. Kortelainen et al.[7] showed that heat treatment decreased the water absorption of spruce and pine heartwood specimens, although pine sapwood specimens that were heat-treated at temperatures below 230°C revealed higher water absorption. Hakkou et al.[5] found that heat-treated wood specimens showed conformational modifications of wood polysaccharide components leading to lower wettability of wood. The plasticization of lignin and the reorganization of the lignocellulosic polymeric components of wood were also proposed as other explanations for the increased hydrophobic characteristic of heat-treated wood. Boonstra and Tjeerdsma[8] stated that the availability and/or accessibility of the free hydroxyl groups of wood carbohydrates play an important role in the process of water absorption. Depolymerization of the carbohydrates and especially the hemicelluloses in heat-treated wood results in a reduction of the total amount of hydroxyl groups, including the free hydroxyl groups.

Boron compounds have long been used as fungicides and insecticides for wood preservation and are especially effective against termites. Boron-based buffers have also been used as additives in fire-retardant treatments and have been

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found to significantly reduce the severity of thermal degradation.[9,10] Boron compounds reduce the flame spread of wood but may have diverse effects on hygroscopicity. Wood treated with inorganic flame-retardant salts is usually more hygroscopic than is untreated wood, particularly at high relative humidities. Increases in the equilibrium moisture content of such treated wood will depend upon the type of chemical, level of chemical retention, and size and species of the wood involved.[11]

The present study investigated the effects of boric acid (BA) and disodium octoborate tetrahydrate (DOT) on the water absorption of sugi sapwood together with heat treatment performed at either 180° or 220°C for either 2 or 4h. The objectives of this study were: (1) to determine the changes in wood carbohydrates in boron-treated and heat-modified wood specimens, and (2) to measure water absorption of the specimens.

Materials and methods

Wood specimens, preservative, and heat treatments

Wood specimens measuring 5 (T) × 10 (R) × 100 (L) mm were cut from sapwood portions of sugi (*Cryptomeria japonica* D. Don). These specimens had been originally prepared for use in tests concerning biological resistance, leaching, and mechanical tests. Prior to the treatments, all wood specimens were conditioned at 20°C and 65% relative humidity (RH) for 2 weeks. The specimens were free of knots and visible concentrations of resins, and showed no visible evidence of infection by mold, stain, or wood-destroying fungi. All specimens were numbered and weighed to the nearest 0.001g before preservative treatments with either boric acid (BA) or DOT solutions. The wood specimens were treated with 5% aqueous solutions of BA and DOT. In the treatments, the pressure cycle consisted of a 30-min period of vacuum (88kPa absolute pressure) in a treatment desiccator. After the treatments, the specimens were reweighed to determine BA and DOT retention. All the treated specimens were then reconditioned at 20°C and 65% RH for 2 weeks. In the study, "untreated wood" refers to wood specimens without any chemical or heat treatment; however, preservative treatments and heat treatments should be considered as different procedures. Heat treatment was performed at either 180° or 220°C for either 2 or 4h using a temperature-controlled laboratory oven.

Analysis of wood carbohydrates

Carbohydrate analyses were performed according to the method described by Davis.[12] For chemical analyses, wood specimens from each treatment group were ground and screened through 40–100 mesh. The ground wood was reacted with 72% sulfuric acid and 40% hydrobromic acid according to the method described by Runkel and Wilke.[13] The carbohydrate contents of the hydrolysates were determined by anion-exchange high-performance liquid chromatography (HPLC) using pulsed amperometric detection. Wood carbohydrates were quantified using an internal standard method and the results were reported in terms of the percentage of the original sample mass.

Water absorption

Wood specimens were placed in glass containers (150mm diameter, 60mm deep) filled with distilled water. The specimens were placed separately and horizontally in the containers with stainless steel mesh over the specimens. The water was replaced daily during the test. The specimens were first oven-dried at 103°C and then weighed. The specimens were weighed after 6, 24, 48, 72, 96, and 148h of immersion and water absorption (*WA*) was calculated as an index of bulking efficiency according to the formula below:

$$WA(\%) = [(W_2 - W_1)/W_1] \times 100$$

where W_2 is the weight of the water-saturated specimen and W_1 is the weight of the oven-dried specimen.

Results and discussion

The boric acid and DOT retention levels of the specimens are given in Table 1. On average, nearly 40 kg m^{-3} retention was obtained in all treated specimens after boron treatments. Figure 1 describes the results of the carbohydrate analyses, showing that heat modification treatments at 180°C for 4h and 220°C for 2 and 4h resulted in remarkable decreases in hemicelluloses. In the specimens exposed to heat treatments at 220°C for 4h, all rhamnan was degraded and the arabinan contents of the same specimens decreased by 90%, 87%, and 84% for untreated, BA-treated, and DOT-treated specimens, respectively, in comparison with untreated and unheated specimens. In the BA-treated and heat-treated specimens at 220°C for 4h, mannan, xylan, and galactan were the least affected hemicellulose group. Of all the specimens treated at 220°C for 4h, glucan was the most resistant to heat degradation. Reductions in glucan content were 10% and 12% in the untreated and BA-treated specimens. However, 34% of the glucan in the DOT-treated specimens was degraded after heat treatments of 220°C for

Table 1. Boric acid (BA) and disodium octoborate tetrahydrate (DOT) retention in the specimens

Concentration (%)	Heat temperature (°C)	Heating time (h)	Dry salt retention (kg m^{-3})
BA 5%	180	2	39.50 (0.61)
BA 5%	180	4	39.88 (0.74)
BA 5%	220	2	39.49 (0.88)
BA 5%	220	4	40.06 (0.80)
DOT 5%	180	2	40.14 (0.73)
DOT 5%	180	4	40.19 (1.06)
DOT 5%	220	2	40.35 (0.65)
DOT 5%	220	4	39.53 (0.88)

Figures in parentheses are standard deviations

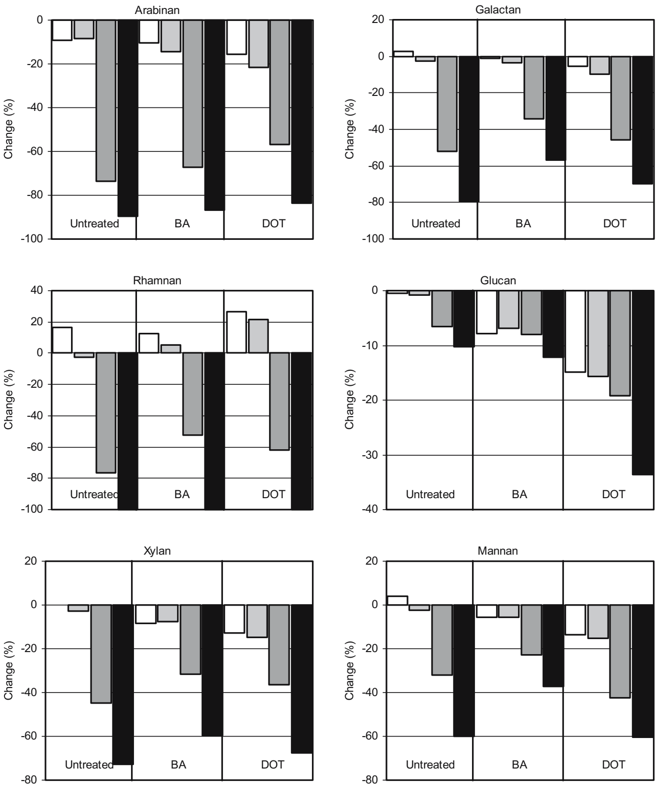

Fig. 1. Changes in carbohydrates contents (arabinan, galactan, rhamnan, glucan, xylan, and mannan) compared with untreated and unheated wood specimens. *Open columns*, 180°C, 2h; *lightly shaded columns*, 180°C, 4 h; *darkly shaded columns*, 220°C, 2 h; *filled columns*, 220°C, 4 h

4 h when compared with untreated and unheated specimens. A study by Sweet and Winandy[14] showed that the arabinose, galactose, xylose, and mannose contents of southern pine dried at 66°C for 560 days decreased by about 50% or more compared with those of untreated wood. Yılgör et al.[15] found that steaming beech wood at 80°C for 20 and 100 h caused small decreases in hemicelluloses. The decrease rates for arabinose, galactose, rhamnose, and mannose in the 100-h steamed wood compared with untreated wood were 9.3%, 7.7%, 7.7%, and 4.8%, respectively. LeVan and Winandy[16] reported that the degradation of hemicelluloses most closely follows the degradation of wood; thus, the lower degradation temperature of wood compared with the lignin degradation temperature is due to the hemicellulose in the wood. They also suggested that when wood is subjected to acidic solutions, which may cause the catalytic action of the cation, carbohydrates are hydrolyzed by cleavage of the glycosidic linkages within polysaccharide chains; however, the possible reaction in the lignin is condensation. Boonstra and Tjeerdsma[8] also stated that polycondensation reactions, which result in further crosslinking of the lignin network, contribute to the increase of the lignin content and that the effect of heat treatments on cellulose is relatively limited, although some depolymerization of the cellulose occurs. Awoyemi and Westermark[10] stated that boron-based buffers may reduce the severity of thermal degradation; however, it is important to know the

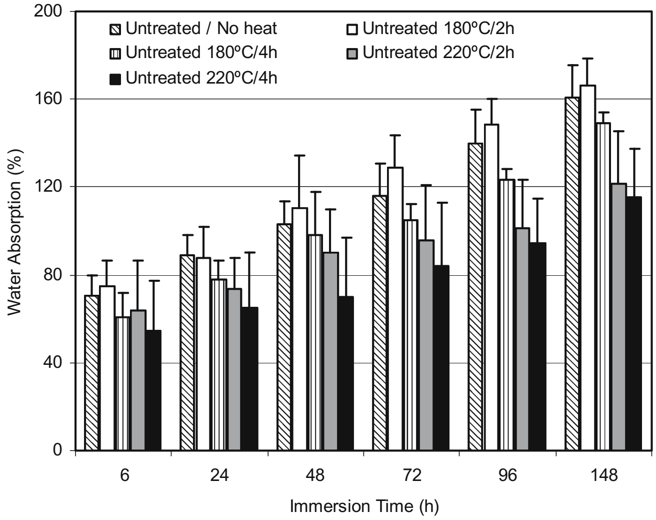

Fig. 2. Water absorption of untreated wood specimens

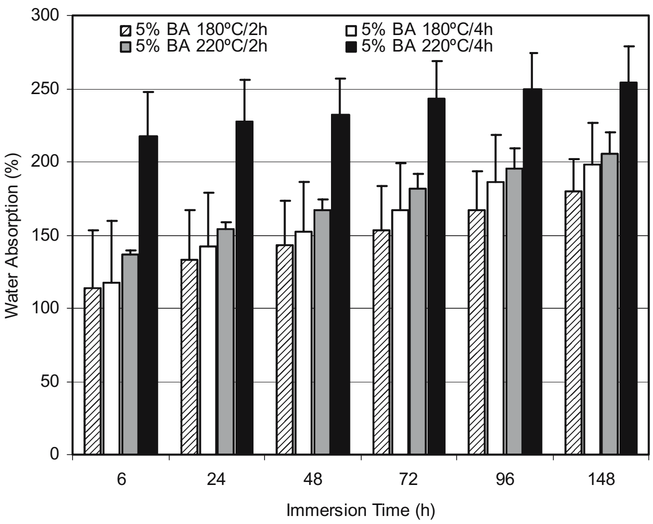

Fig. 3. Water absorption of boric acid (BA)-treated wood specimens

presence of alkali or acidic material in the wood because degradation of wood components is closely correlated with decreased or increased acidity.

The water absorption contents of the specimens during the immersion tests are shown in Figs. 2, 3, and 4. Each column represents the average of ten replications for each treatment group. In general, the water absorption of untreated and heat-modified specimens decreased as the temperature and time increased, with the exception that the specimens heat treated at 180°C for 2 h showed higher water absorption. More interesting results were obtained in the specimens treated with the boron compounds. The water absorption of these specimens increased with temperature and time. The increases were slight in the specimens treated at 180°C for 2 and 4 h and 220°C for 2 h. However, the water absorption in the specimens treated at 220°C for 4 h was considerably higher. The specimens treated with DOT showed water absorption content similar to BA-treated

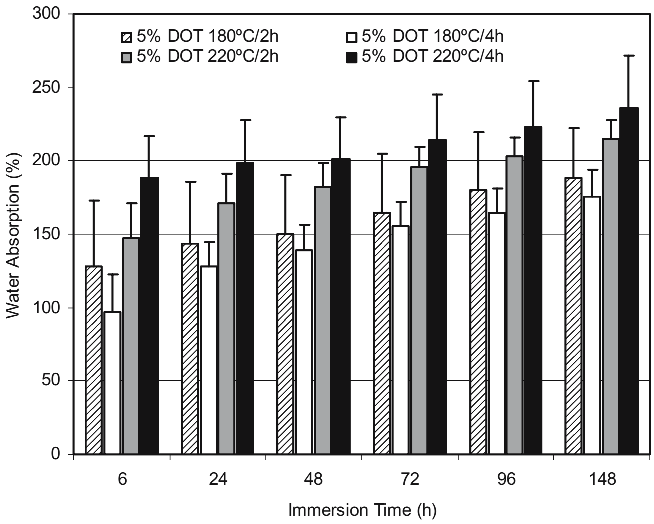

Fig. 4. Water absorption of disodium octoborate tetrahydrate (DOT)-treated wood specimens

specimens, although the specimens treated at 220°C for 4h absorbed remarkably less water in comparison with BA treatments. In the DOT treatments, the specimens treated at 180°C for 4h showed slightly less water absorption than the rest of the specimens. These results suggest that boron compounds may affect the water absorption of heat-modified wood even though heat treatments result in hydrophobication, and, in turn, decreased water absorption. The hygroscopic structure of boron compounds affects the amount of water absorbed by wood under high humidity conditions or during service.

Conclusions

Heat-modified wood showed decreased water absorption when compared with unheated wood. However, boron content in the modified wood caused increased water absorption due to the hygroscopicity of BA and DOT. In the heat treatments, hemicellulose degradation was almost identical in untreated, BA-treated, and DOT-treated specimens. These results suggest that the heat treatment of boron-treated wood may result in increased hygroscopicity, which suggests the limited use of boron and heat-treated wood under humid service conditions. Further studies are in progress to determine if other wood preservatives or fire-retardant chemicals affect the moisture content of heat-modified wood and to understand the mechanism of water uptake in boron and heat-modified wood.

Acknowledgments This study was performed during the first author's short visit to the Research Institute for Sustainable Humanosphere (RISH), Kyoto University, Kyoto, Japan, and was financially supported by the same institute. The authors gratefully acknowledge Ms. Carol A. Clausen of USDA Forest Service Forest Products Laboratory, Madison, WI, USA, for lignin and carbohydrate analyses of wood specimens.

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