DENSIFICATION OF WOOD VENEERS COMBINED WITH OIL-HEAT TREATMENT. PART III: CELL WALL MECHANICAL PROPERTIES DETERMINED BY NANOINDENTATION

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Compression under the effect of heat and steam, also called thermo-hygromechanical (THM) densification, can increase wood density and therefore improve its strength, stiffness, and hardness. Oil-heat treatment (OHT) is also known to reduce wood's hygroscopicity and improve dimensional stability. A combination of both treatments can therefore produce wood with improved mechanical properties and dimensional stability. The objective of this project was to determine cell wall mechanical properties of THM-densified and OHT wood. Trembling aspen veneers were densified by a THM process and subsequently treated in canola oil at 200 and 220°C. Nanoindentations were performed in earlywood cell walls. The results show that cell wall longitudinal modulus of elasticity increased significantly from 13.5 GPa for the control to a maximum of 18.2 GPa for THM densified wood with or without OHT. Cell wall hardness increased from 0.27 GPa to a maximum of 0.43 GPa. Both THM densification and OHT significantly increased cell wall hardness. Therefore, the increase in mechanical properties of THM-densified and OHT wood can be due to an increase in wood density resulting from a reduction in porosity but also to an increase in the mechanical properties of the cell wall.

Keywords: Densified wood; Mechanical properties; Cell wall; Nanoindentation; Oil-heat treatment; Aspen

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INTRODUCTION

Wood mechanical properties are generally correlated with density. Many wood densification processes have been developed to enhance mechanical and physical properties (Navi and Heger 2004; Kamke 2006; Inoue et al. 2008; Fang et al. 2011, 2012a,b). These processes increase wood density by compressing wood to reduce void volume, by impregnating the void volume with a fluid substance, or by using a combination of compression and impregnation. However, unlike physical or mechanical compression, chemical impregnation affects the natural and sustainable character of wood, and is usually expensive (Navi and Heger 2004). Mechanical compression processes have been reported for over a century. However, this type of compressed wood is unstable, recovering its original shape almost completely when re-moistened and heated. In order to improve dimensional stability, compression combined with steam and heat has been receiving more attention. Various densification processes combined with steam and heat have been attempted (Higashihara et al 2000; Navi and Heger 2004; Kamke 2006; Fukuta et al 2008; Inoue et al 2008; Gabrielli and Kamke 2010). Some of these still cannot solve the problem of dimensional stability. Other processes are lengthy or complex and limited to batch processes. Furthermore, most deal with small wood samples.

The boiling point of many natural oils is higher than the temperature required for the heat treatment of wood. This opens the way for the development of several heat treatments of wood in an oil bath. Oil-heat treatment (OHT) has been developed in Germany (Sailer et al 2000; Welzbacher and Rapp 2002; Manalo and Acda 2009). This type of treatment is carried out in a closed vessel, with hot crude vegetable oil circulating around the wood during treatment. The hot oil is used for fast and homogeneous heat transfer to the wood in the absence of oxygen. Some of the oil also penetrates into the wood, reducing water absorption in service. The process is simple and emission-free since it is carried out in a closed system. Temperature control of oil is easy, and no positive pressure is involved. In a previous study, OHT was successfully applied to wood densified by the thermo-hygromechanical (THM) process (Fang et al. 2011, 2012a).

Wood mechanical properties are well understood at the macroscale level. However, little information is available at the microscale and nanoscale levels, including the cell wall and its constituent mechanical properties. The nanoindentation technique determines the mechanical properties of a material at the submicron and nanoscale level. This method involves the penetration of a tip (indenter), while the penetration depth and load are recorded. The stiffness and hardness of the indented zone can then be calculated. Therefore, the mechanical properties of the cell wall can be determined accurately (Wimmer et al. 1997; Gindl and Schöberl 2004; Gacitúa et al. 2007; Xing et al. 2009; Yin et al. 2011).

Our previous work (Fang el al. 2012a) has shown that THM densification increases Brinell hardness, tensile strength, and bending strength of trembling aspen (*Populus tremuloides*) wood significantly and OHT improves its dimensional stability. However, it was not clear whether the increase in mechanical properties is due to the increase in wood density resulting from a reduction in porosity, or to an additional effect from a modification of the cell wall material. The nanoindention technique can be used to determine the effect of THM densification and OHT on wood cell wall mechanical properties. The objective of this study was to determine cell wall properties of THM-densified and OHT trembling aspen veneers by nanoindentation.

MATERIALS AND METHODS

Materials

Rotary-peeled aspen wood veneers were obtained from Temlam Inc., a laminated veneer lumber plant in Amos, which is located in the northwest of the province of Quebec, Canada. The nominal thickness of the aspen veneers was 3.2 mm. Veneers were conditioned at 20°C and 60% relative humidity (RH) before densification.

Densification and Oil-heat Treatments

Veneers of 700 mm × 700 mm were densified using pressure, heat, and steam, also known as the THM process, as described in our previous work (Fang et al 2011). The theoretical compression was set at 50%. Veneers were densified at 200 and 220°C. After THM densification and before OHT, the veneers were conditioned at 20°C and 60% RH until their weight became stable. As a result of the THM densification process, the veneers' average oven-dry density increased from 388 to 812 kg/m^3.

Veneer samples (50 × 50 mm) densified at 200ºC were cut from the densified veneers with a laser cutter. They were treated in hot canola oil at 200 and 220 ºC for 2 hours (specific gravity 0.91, viscosity 78.2 cSt, smoke point 220-230 ºC). The samples were immersed in pre-heated canola oil as temperature was maintained at the target temperature. As all the samples were thin and small, their internal temperature could reach the target temperature quickly and uniformly. The samples were then taken out from the hot oil vessel, and the oil remaining on the surface was removed with a paper cloth. The OHT samples were conditioned at 20°C and 60% RH until their weight became stable.

Nanoindentation Procedure

A Hysitron Triboindenter® equipped with a three-sided pyramid Cube corner diamond indenter tip located at the Nanotechnology Laboratory of the Universidad del Bío-Bío, Concepción, Chile was used to determine the mechanical properties of the fiber cell walls. Five treatments were studied: non-densified (control), densified at 200ºC without OHT, densified at 220ºC without OHT, densified at 200ºC with OHT at 200ºC and densified at 200ºC with OHT at 220ºC. For each of the five treatments considered, two 50 × 50 mm veneer samples were used for nanoindentation. From each veneer sample, a 3 × 3 × 3 mm specimen was cut and embedded with Spurr epoxy resin. Axial indentations were performed in earlywood fibers of the veneer samples across the transverse surface of the secondary cell wall.

A loading function was applied to load a peak force of 100 μN for 60 s with loading and unloading performed at 20 μN/s. In a given indentation experiment, the peak load (P_{max}), the penetration depth at peak load (h) and the initial slope of the unloading curve (S=dP/dh) were obtained. From the indenter geometry and h, the projected contact area (A) was calculated. The load-displacement data from the nanoindentation test were used to calculate hardness (H) and elastic modulus (E_s) of the cell wall at the indentation location.

The hardness (H) of the samples for an indentation depth (h) can be calculated from the following equation:

$$H = \frac{P\max}{A} \tag{1}$$

The combined modulus of the system, or reduced indentation modulus (E_r) was determined from the following expression,

$$E_r = \frac{1}{2}\frac{dP}{dh}\frac{\sqrt{\pi}}{A} \tag{2}$$

where d*P*/d*h* is the slope of the tangent to the initial unloading curve in the load–displacement plot (Fig. 1). The sample modulus (E_s) can then be calculated as follows (Oliver and Pharr 1992),

$$E_s = (1-\nu_s^2)\left(\frac{1}{E_r} - \frac{1-\nu_i^2}{E_i}\right)^{-1} \tag{3}$$

where the sub-indexes “s” and “i” represent the sample (cell wall, S2 layer) and indenter, respectively, and v is the Poisson’s ratio.

The indenter modulus E_i is constant and equal to 1140 GPa, with a Poisson’s ratio of 0.07. A Poisson’s ratio of 0.30 was assumed for trembling aspen. Between 25 and 65 indents were performed in the S2 layer of the fiber cell wall for each specimen. The specimens were placed in the nanoindenter cabinet at room conditions for the duration of the measurements.

A one-way analysis of variance (ANOVA) was carried out using the SPSS software. A Student-Newman-Keuls test for pairwise comparison of subgroups was performed to test the difference between the treatment means.

RESULTS AND DISCUSSION

Typical nanoindentations in fiber cell walls of trembling aspen densified at 220°C without OHT are presented in Fig. 2. A summary of test results showing the average and standard deviations of the cell walls E_s values obtained is given in Table 1. The average E_s obtained for non-densified (control) wood (13.5 GPa) is comparable to the average E_s value obtained by Weimmer et al. (1997) for red spruce earlywood tracheid tangential walls (13.49 GPa).

The analysis of variance shows that densified wood cell wall with or without OHT exhibited a higher E_s than non-densified (control) wood. The E_s of the cell wall was also affected by OHT. It increased slightly from 15.0 GPa to 17.5 GPa for wood densified at 200°C and subsequently OHT at 200°C. These values are significantly different from those of non-densified (control) wood cell walls, averaging 13.5 GPa. Densification at 200ºC without OHT resulted in a significantly lower E_s of the cell wall (15.0 MPa) than densification at the same temperature with OHT (17.5 MPa) or densification at 220ºC without OHT (18.2 MPa). This shows that both THM densification and OHT increase E_s of the cell wall. However, no significant differences were found between cell wall E_s of wood densified at 200ºC with OHT at 200 and 220ºC (17.5 and 18.2 MPa), and with wood densified at 220ºC without OHT (18.2 MPa).

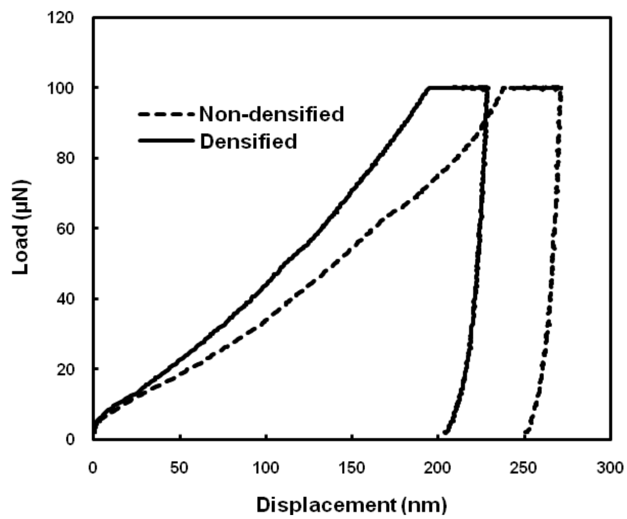

Fig. 1. Typical load-displacement curves of nanoindentations in fiber cell walls of trembling aspen non-densified without oil-heat treatment (control) and densified at 200°C with oil-heat treatment at 220°C

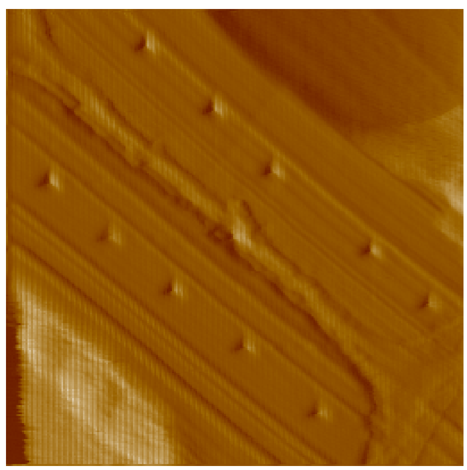

Fig. 2. Typical nanoindentations in fiber cell walls of trembling aspen densified at 220°C without oil-heat treatment

A summary of test results showing the averages and standard deviations of fiber cell wall hardness is given in Table 1. The average *H* obtained for non-densified (control) wood (0.27 GPa) is comparable to the average *H* value obtained by Weimmer et al. (1997) for red spruce tracheid tangential walls (0.28 GPa). Cell wall hardness appears to be related to the amount of heat applied during the THM densification process and OHT. The analysis of variance shows that there were significant differences between the *H* values of cell walls from non-densified (control) wood (0.27 GPa) and 3 out of the 4 treatment combinations: densified at 220°C without OHT (0.33 GPa), densified at 200°C with OHT at 200°C (0.35 GPa), and densified at 200°C with OHT at 220°C (0.43 GPa) (Table 1). Fiber cell wall *H* increased from 0.27 GPa for the control to 0.43 GPa for wood densified at 200°C and OHT at 220°C, corresponding to an increase of 59%. This can partially explain the increase in *H* of about 190% measured at the macroscopic scale following THM densification of trembling aspen veneers by Fang et al. (2010, 2012a).

Table 1. Trembling Aspen Densified and Oil-heat Treated (OHT) Veneer Earlywood Cell Walls Elastic Modulus (E_s) and Hardness (H)

Statistical parameter	Non-Densified (Control)	Densified at 200°C without OHT	Densified at 220°C without OHT	Densified at 200°C with OHT at 200°C	Densified at 200°C with OHT at 220°C
Mean E_s (GPa)	13.5^{A}*	15.0^{B}	18.2^{C}	17.5^{C}	18.2^{C}
Std. dev. (GPa)	2.3	2.9	4.2	2.8	3.6
n	48	36	65	56	25
Mean H (GPa)	0.27^{A}*	0.28^{A}	0.33^{C}	0.35^{D}	0.43^{E}
Std. dev. (GPa)	0.02	0.03	0.03	0.02	0.06
n	46	35	64	57	25

n: Sample size (number of indentations).
*: Means with the same letter are not significantly different at the 5% probability level.

Yin et al. (2011) reported the effect of steam treatment without densification on the properties of Norway spruce (*Picea abies*) wood cell wall determined by nanoindentation. Their results show a decreasing trend of the average H of the cell wall with an increase in the steam treatment temperature. The decomposition of the cell wall hemicelluloses and lignin was mentioned as a potential cause for the reduced H. On the other hand, Diouf et al. (2011) reported that aspen wood densified by the THM process at temperatures between 160°C and 220°C shows cell wall hemicelluloses cleavage and alteration but also a new lignin complex formed. This effect combined to the mechanical densification might explain the increase in E_s and H observed in the current study.

CONCLUSIONS

1. The longitudinal modulus of elasticity of the cell wall increased significantly from 13.5 GPa for the control to a maximum of 18.2 GPa for thermo-hygromechanical densified wood with or without oil-heat treatment.
2. Cell wall hardness increased from 0.27 GPa for the control to a maximum of 0.43 GPa for densified wood with oil-heat treatment at 220°C.
3. Both thermo-hygromechanical densification and oil-heat treatment significantly increased cell wall axial modulus of elasticity and hardness.
4. The increase in mechanical properties of thermo-hygromechanical densified and oil-heat treated wood reported in Fang et al. (2012a) results from increased wood density and also from increased cell wall mechanical properties.

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