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Effect of compression combined with steam treatment on the porosity, chemical compositon and cellulose crystalline structure of wood cell walls

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ABSTRACT

The changes of porosity, chemical composition and cellulose crystalline structure of Spruce (*Picea abies* Karst.) wood cell walls due to compression combined with steam treatment (CS-treatment) were investigated by nitrogen adsorption, confocal Raman microscopy (CRM) and X-ray diffraction (XRD), respectively. A number of slit-shaped mesopores with a diameter of 3.7 nm was formed for the CS-treated wood, and more mesopores were found in the steam-treated wood. CRM results revealed cellulose structure was affected by treatment and β-aryl-ether links associated to guaiacyl units of lignin was depolymerized followed by re-condensation reactions. The crystallinity index (CrI) and crystallite thickness (D_{200}) of cellulose for CS-treated wood were largely increased due to crystallization in the semicrystalline region. Higher degree of increase in both CrI and D_{200} was observed in both the earlywood and latewood of steam-treated wood, ascribing to the greater amount of mesopores in steam-treated wood than CS-treated wood.

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1. Introduction

Wood is the most abundant natural and renewable materials on earth, and has a long history to be widely used for construction, furniture and packaging industry. However, the utilization of wood, especially the plantation wood, is restricted by its inherent limitations in its properties, such as poor dimensional stability and durability, low density and strength (Drafz, Franz, Namyslo, & Kaufmann, 2015; Wei, Stark, & McDonald, 2015; Wikberg & Maunu, 2004). Considerable wood modification technologies were attempted in order to improve the performances of wood based materials. Great efforts are devoted to develop more environmentally benign and efficient modification methods (Fang, Mariotti, Cloutier, Koubaa, & Blanchet, 2012). Among them, compression combined with steam treatment (CS-treatment, or thermo-hydro-mechanical treatment) was able to improve the dimensional stability, durability as well as the mechanical strength of wood without deteriorating its advantages (Kutnar & Kamke, 2012). During CS-treatment, high temperature steam with more effective heat transfer than conventional heat treatment was applied to obtain a permanent fixation of compressive deformations. This can overcome the problem of typical compression treated wood that the compressive deformation is unstable and the structure can be easily recovered (completely/partially) after reheating and water/moisture exposure (Dwianto, Morooka, & Norimoto, 2000; Kekkonen, Ylisassi, & Telki, 2014). Hence, CS-treatment could transform wood into a new material with desired stability (Popescu, Lisa, Froidevaux, Navi, & Popescu, 2014).

Significant strides have been made in elucidating the changes in the macroscopic characteristics e.g., color and shape, dimensional stability and mechanical properties of wood materials after CS-treatment (Cai, Yang, Cai, & Sheldon, 2013; Inoue, Norimoto, Tanahashi, & Rowell, 1993; Lesar, Humar, Kamke, & Kutnar, 2013; Navi & Girardet, 2000). However, it was unclear about the mechanism caused by steam degradation and the rearrangement of bio-molecules under compressive condition. Changes in physical and chemical structure on a molecular level have not been fully characterized and understood. It is therefore desirable to monitor

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the decomposition of the polymer structure in the cell wall and gain knowledge of property changes in CS-treated wood.

In addition, wood is a cellular biomaterial with complex multi-component structure. The cell wall is primarily comprised of cellulose, hemicellulose and lignin. Cellulose molecules form microfibrils aggregates that are embedded in a soft matrix of hemicellulose and lignin (Salmén & Burgert, 2009). The properties of wood are highly dependent on the chemical compositions, the orientation of cellulose microfibrils, and the molecular interactions of the cell wall polymer assembly (Burgert, 2006; Wei & McDonald, 2016).

In our previous studies (Guo, Song, Salmén, & Yin, 2015 Yin, Berglund, & Salmén, 2011), it was shown that CS-treatment and steam treatment led to the changes of chemical components, especially hemicelluloses, in wood cell walls. Specifically, a progressive degradation of the carbonyl groups in the glucuronic acid unit of xylan and the mannose units in the glucomannan would occur. This resulted in the decrease of moisture absorbing sites and the linkages among the polymers in the wood cell wall, which are wholly accounted for changes of the hygroscopicity and indentation modulus of the wood cell wall. However, the degradation pathways of cellulose and lignin have not been clarified. It is known that the origins of cellulose molecular chains, such as the crystalline, semicrystalline and amorphous regions, have various effects on the characteristics of wood (Inagaki, Siesler, Mitsui, & Tsuchikawa, 2010). In addition, the crystalline regions of cellulose exhibit higher density and lower chemical reactivity, and can determine the mechanical properties of plant cell wall (Wei, McDonald, & Stark, 2015; Wei & McDonald, 2016). Moreover, each glucopyranose ring of cellulose has three hydroxyl groups on average, implying cellulose is highly hydrophilic material (Kulasinski, Guyer, Keten, Derome, & Carmeliet, 2015; Wei, Liang, & McDonald, 2015). Lignin is biosynthesized from three basic monomeric units, syringyl, guaiacyl, and *p*-hydroxyphenyl alcohol. Lignin is a highly amorphous macromolecule that plays an important role of supporting material in wood cell wall (Song, Yin, Salmén, Xiao, & Jiang, 2014).

Therefore, gaining more knowledge about the structure of cellulose and lignin should provide insight into the mechanism of cell wall changes responding to CS-treatment. Furthermore, wood cell walls exhibit large mesopores because the spaces between the cellulose microfibrils could be partially filled by lignin, hemicellulose and extractive (Yin, Song, Lu, Zhao, & Yin, 2015). The structure of mesopores in wood cell wall could affect the sorption and transport of moisture. Any changes in the mesopore structure due to CS-treated modification could determine the properties of modified wood.

In this paper, the effects of CS-treatment on porosity, chemical composition and cellulose crystalline structure on a molecular level were studied in details. Nitrogen adsorption was studied for the mesopore structure upon treatments. Confocal Raman microscopy (CRM) was used to investigate the chemical composition distribution in wood cell wall including the secondary cell walls (S) and cell corners (CC). X-ray diffraction (XRD) was used to characterize the cellulose crystalline structure. Differences between the earlywod and latewood were explored as well. The results would promote the understanding of the effect and mechanism of degradation and rearrangement of chemical composition, especially cellulose, during CS-treatment.

2. Experimental

2.1. Materials

Small specimens (dimensions were 20 × 20 × 25 mm in the tangential (T), radial (R), and longitudinal (L) directions, respectively) cut from Spruce (*Picea abies* Karst.) sapwood section were subjected to CS-treatment in a laboratory-scale autoclave as described in our previous studies (Guo et al., 2015). To be more specific, the CS-treatment was conducted with a compression ratio of 50% in radial direction (the percentage of the decrease in thickness to the initial thickness of the specimen) at 110 °C for 6 min, followed by a steaming process at 160 °C for 30 min. For comparison, specimens were treated with steam only without using compression treatment in the autoclave at 160 °C for 30 min. All the treated samples were put into a preheated autoclave, with pressurized steam being applied to regulate the corresponding prescribed temperature. The treated samples were cooled down to room temperature inside the autoclave and then conditioned to an equilibrium moisture content close to 12% by storing them in a conditioning room maintained at 20 °C and 65% relative humidity for >20 days.

Small wood pieces containing whole growth rings with an age of 30 years were cut from the surface of the treated samples and then seperated into five samples, see Fig. S1 (Supplementary). Sample 1 (S1) was divided into earlywood and latewood with aid of a stereo-microscope (S6E, Leica, Germany) and then cut into wood sticks (5 mm in longitudinal direction, 1 × 1 mm^2 in cross section) for nitrogen adsorption measurement. Sample 2 (S2) was sliced in radial directions (200 μm thickness) for examination with a field emission scanning electron microscope (FE-SEM). Sample 3 (S3) was sliced in radial directions (10 μm thickness) for atomic force microscope (AFM). Sample 4 (S4) was sliced in cross sections (10 μm thickness) for CRM analysis. Earlywood and latewood of Sample 5 (S5) were isolated in the same way as S1, and then were milled into powder for X-ray diffraction (XRD) measurement.

2.2. Nitrogen adsorption

The samples were supercritically dried using a critical point drier (EM CPD300, Leica, Germany). More specifically, wood sticks were firstly dehydrated using a series of ethanol with different concentration, 80%, 90%, 95%, and 100%. The dehydrated samples were introduced into the drier apparatus, which was filled with liquid carbon dioxide. During supercritical drying, the liquid carbon dioxide was transformed into a supercritical fluid with a null surface tension. When the temperature was increased beyond its critical point (304.25 K at 7.39 MPa), the valve of the drier was gradually opened to allow gas to escape. In this way, shrinkage due to capillary pressure was avoided.

Nitrogen adsorption test was carried out using a surface area and pore-size analyzer (Autosorb iQ, Quantachrome, USA) at 77 K. Before the adsorption measurements, samples (1.0 g–1.5 g) were degassed at 80 °C for 10 h under a high vacuum (<10^{-5} Pa) to remove any moisture or adsorbed contaminants from sample surfaces. By means of the nitrogen adsorption isotherms, pore volume was derived from the amount of adsorbed nitrogen at a relative pressure close to unity, assuming the pores were filled with liquid adsorbate. Shapes of pores were calculated using the hysteresis loops. The total pore volume (V_{total}) was calculated from the volume of the liquid nitrogen, maintained at the relative pressure of 0.99. The Brunauer-Emmett-Teller (BET) surface area (S_{BET}) of the samples was determined using an accelerated surface area (Brunauer, Emmett, & Teller, 1938). The pore-size distribution was calculated using the Barrett-Joyner-Halenda (BJH) method (Barrett, Joyner, & Halenda, 1951).

2.3. Field emission scanning electron microscope (FE-SEM)

The morphology of samples was examined by FE-SEM (JSM-6301F, JEOL, Japan) with a secondary electron detector operating at 5 kV–10 kV. Radial section of wood samples were cut and super-

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