Carbohydrate Polymers 115 (2015) 207–214

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Changes of wood cell walls in response to hygro-mechanical steam treatment

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ARTICLE INFO

Article history:
Received 1 April 2014
Received in revised form 6 August 2014
Accepted 9 August 2014
Available online 27 August 2014

Keywords:
Cell wall
Hygro-mechanical steam treatment
Earlywood
Latewood
Biopolymer components

ABSTRACT

The effects of compression combined with steam treatment (CS-treatment), i.e. a hygro-mechanical steam treatment on Spruce wood were studied on a cell-structure level to understand the chemical and physical changes of the secondary cell wall occurring under such conditions. Specially, imaging FT-IR microscopy, nanoindentation and dynamic vapour absorption were used to track changes in the chemical structure, in micromechanical and hygroscopic properties. It was shown that CS-treatment resulted in different changes in morphological, chemical and physical properties of the cell wall, in comparison with those under pure steam treatment. After CS-treatment, the cellular structure displayed significant deformations, and the biopolymer components, e.g. hemicellulose and lignin, were degraded, resulting in decreased hygroscopicity and increased mechanical properties of the wood compared to both untreated and steam treated wood. Moreover, CS-treatment resulted in a higher degree of degradation especially in earlywood compared to a more uniform behaviour of wood treated only by steam.

1. Introduction

Wood is one of the oldest composite structures man has made use of, in which thousands of primary structure building blocks of tracheids or fibres packed orderly together. In softwoods, about 94% of the wood cells are tracheids (Havimo et al., 2007). Earlywood tracheids, with a thinner wall and wider lumen, and latewood tracheids, with a much thicker wall and narrow lumen, can be observed in an integrated growth ring (Richter et al., 2004; Panshin & Zeeuw, 1970). The wood cell wall is even more structurally advanced, whose structure is principally composed of cellulose microfibrils embedded in a matrix composed of lignin and hemicelluloses (Fengel & Wegener, 1984).

As a renewable resource with an exceptional strength-to-weight ratio, the utilization of wood is restricted by the lack of dimensional stability, low resistance to decay, and poor durability (Hill, 2006). Thus there has recently been a renewed interest in wood modification. Among the various techniques for improving the quality of wood, wood densification (Kollmann et al., 1975; Inoue et al., 1990; Kutnar & Šernek, 2007; Homan & Jorissen, 2004) has been thought to be a promising method, aiming to acquire desired functionality without changing the advantages of wood. Densification undoubtedly improves certain mechanical and physical properties of wood but the transformed shape (compression deformation) produced during densification is unstable and is easy recovered totally or partially after re-moistening and heating.

Until now, large efforts in chemical modification (Ermeydan et al., 2012; Trey et al., 2010; Ermeydan et al., 2014; Deka & Saikia, 2000; Jebrane et al., 2011; Yuan et al., 2013; Jebrane & Sèbe, 2008) have been devoted to maintain permanent fixation of wood materials. Hydro-thermal treatment (Esteves & Pereira, 2009; Todaro et al., 2012; Lam et al., 2013; Tooyserkani et al., 2013) and thermo-hygro-mechanical treatment (Navi & Girardet, 2005; Welzbacher et al., 2008; Diouf et al., 2011; Cai et al., 2013) remain challenging and attractive since they are efficient and ecofriendly strategies to improve the dimensional stability and durability of wood.

However, the influence and mechanisms of the steam degradation process and rearrangement of biomolecules under compressive condition, with regard to changes in the chemical structure and in the mechanical properties on a cellular level, have not been fully characterized and understood. In a previous paper

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http://dx.doi.org/10.1016/j.carbpol.2014.08.040
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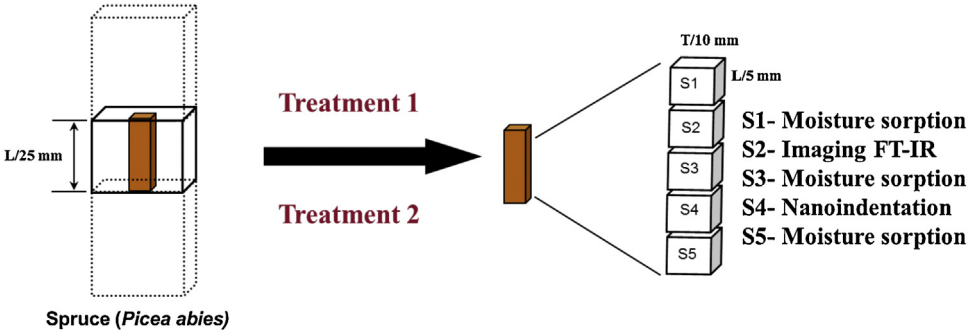

Fig. 1. Scheme of preparation of wood samples for Imaging FT-IR, moisture sorption, and nanoindentation measurements. Treatment 1: the CS-treatment; Treatment 2: high-temperature steam treatment.

(Yin et al., 2011), we reported effects of high-temperature steam treatment on the chemical and physical changes of softwood on a cell-structure level. It was indicated that chemical changes in the biopolymer components of the cell wall could fully account for the changes observed in the hygroscopicity and indentation modulus of the wood material while no major difference was detected between the effects of the steam treatment on earlywood and latewood.

In this paper, the effects of compression together with a hygrothermal treatment were studied on the chemical and physical changes of Spruce (*Picea abies* Karst.) on a cell-structure level (the term "hygro" refers to treatments using water steam (e.g. high pressure steam) as compared to the term "hydro" which is used to describe treatments using water). Specifically, imaging FT-IR microscopy was utilized to track the variations in chemical structures under compression combined with steam treatment (CS-treatment) on a micrometer level. Moreover, nanoindentation, a method of mechanical testing on a submicrometer scale that highlights structural variations in biomaterials, such as wood and bamboo (Ermeydan et al., 2012; Vincent et al., 2014; Gindl et al., 2004; Gershon et al., 2010; Yu et al., 2007; Oliver & Pharr, 1992) was used. Furthermore, the influences on the earlywood and latewood structures were explored. The results would promote the understanding of the effect and mechanism of steam degradation and rearrangement of biomolecules under compressed condition and also provide a scientific basis for the development of environmentally friendly wood products that may have the potential to substitute the wide use of chemical preservatives for wood.

2. Materials and methods

2.1. Materials

Small specimens (dimensions 20 × 20 × 25 mm in the tangential (T), radial (R), and longitudinal (L) directions, respectively) cut from Spruce (*Picea abies* Karst.) wood lumber were treated by CS-treatment. The CS-treatment was conducted with a 50% radial compression ratio (the percentage of the decrease in thickness to the initial thickness of the specimen) at 110 °C for 6 minutes (min) followed by a steaming process at 160 °C for 30 min. All treated specimens were placed in the pre-heated autoclave and pressurized steam was applied and regulated to the corresponding prescribed temperature. The treated specimens were then cooled down to room temperature inside the autoclave and then conditioned to an equilibrium moisture content (EMC) of approximately 12%, by storing in a constant environment room maintained at a constant 20 °C, 65% relative humidity (RH) for at least 20 days. For comparison, specimens were high-temperature steam treated in the autoclave for 30 min at 160 °C as described in a previous study (Yin et al., 2011).

Small wood pieces containing an integrated growth ring were prepared from the surface of the treated samples (Fig. 1A) and then divided into five pieces (Fig. 1B). The specimens represented wood from approximately annual rings of an age of 30 years. One piece was use to slice transverse sections of 20 μm thickness for imaging FT-IR measurement. Three pieces were used for preparation of micro-specimen of the dimensions (10 × 10 × 1 mm) for moisture sorption testing. Each of them represented a dry mass of approximately 50 mg. One piece was divided into approximately 2 mm long sticks and embedded after freeze drying into Spurr epoxy resin for nanoindentation testing. Similarly, specimens of native spruce wood were prepared as reference materials.

2.2. Microscopic observations

Embedded wood samples were polished across the tracheids using a fine grinder to prepare the surfaces so that their quality would be suitable for microstructure observations under a stereomicroscope before nanoindentation measurement.

2.3. Imaging Fourier transform infrared spectroscopy (FT-IR) microscopy

Chemical changes in the secondary cell wall of tracheids were characterized by imaging FT-IR microscopy in the mid-IR range. The transmission mode was applied on a Spectrum Spotlight 400 imaging FT-IR system (Perkin Elmer Inc., Shelton, CT, USA). From each specimen, three areas of 150 by 150 μm were randomly selected in the earlywood and latewood of a transverse section (Fig. 2A), respectively, using a visible CCD camera. Using a specially designed array detector, scanning was carried out on 16 elements, providing a resolution of 6.25 × 6.25 μm. Eight scans per pixel were added to improve the signal-to-noise ratio (*S*/*N*). The spectra were recorded with 4 cm^{-1} spectral resolution between 4000 cm^{-1} and 720 cm^{-1} and a total full-spectral image (Fig. 2B) of each selected region was then obtained.

The obtained IR spectra were then processed by the software Spotlight 1.5.1, Hyperview 3.2 and Spectrum 6.2.0 developed by Perkin Elmer Inc. The functions of atmosphere correction, flat correction and baseline offset correction were applied in turn to create corrected spectra. Base-line correction was applied at 1800, 1548, 840 and 780 cm^{-1}. Ten pixel positions corresponding to the secondary cell wall in each of the scanning areas were randomly selected for assessing average spectra of each specific area. The spectra were normalized to 1.0 at the cellulose 1425 cm^{-1} peak in order to compare the relative composition in different samples. By focusing on the secondary wall of transverse wood sections the eventual influence on the spectra from redistributed extractives, due to the heat treatment (Yin et al., 2011), was minimized.