



The effect of de- and re-polymerization during heat-treatment on the mechanical behavior of Scots pine sapwood under quasi-static load

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ARTICLE INFO

Keywords:

Chemical composition
Mechanical properties
FT-IR spectroscopy
Scanning electron microscopy
Thermal modification
Wood

ABSTRACT

Loss in strength and ductility is a major drawback for the heat-treatment of solid wood. Previous studies focused mainly on the de-polymerization of cell wall constituents as a cause and the importance of the preferential removal of hemicelluloses. This study tested the hypothesis that the mechanical behavior of wood is additionally affected by re-polymerization reactions within the cell wall matrix during heat-treatment. This was achieved by comparing changes in chemical composition, FT-IR spectra, and mechanical properties of Scots pine sapwood that was heat-treated in either dry state in superheated steam or in wet state using pressurized hot water. Although preferential de-polymerization of hemicelluloses was evident for both heat-treatment techniques, the analysis of the chemical composition and FT-IR spectroscopy indicated additional re-polymerization reactions within the cell wall matrix of dry heat-treated wood. The consequent formation of covalent bonds and cross-links increased the resistance against compression loads and hindered inelastic deformation during bending. This resulted in an additional reduction in bending strength and strain energy density of dry compared to wet heat-treated wood. Re-polymerization reactions during heat-treatments of wood in dry state were suggested as the main cause for the brittle failure under bending loads, while the effect of hemicellulose-removal on brittleness was much smaller than stated previously.

1. Introduction

When exposed to heat, various chemical reactions take place that change the chemical composition and the structural arrangement of the wood cell wall. Chemical changes caused by heat-exposure are induced intentionally during heat-treatment (HT) of solid wood on industrial-scale. Various industrial HT processes are operated in Europe, which are reviewed in detail by Militz and Altgen [1]. During most HT processes for solid wood, e.g. the ThermoWood® process that has the largest market shares of heat-treated wood produced in Europe [2], temperatures between 160 and 240 °C are applied for several hours to nearly dry wood material. This enables the use of European wood species in exterior applications [1]. However, HT is a balance between improving the dimensional stability [3] and the resistance to decay fungi [4,5] of wood on the one hand, while reducing its strength and ductility on the other hand [6–9]. The latter causes problems in load-bearing applications, and can also be the result of heat-induced chemical changes during re-drying of fire-retardant-treated wood [10], or hot-pressing of wood composites [11]. Despite the many investigations dealing with the change in the macro-scale mechanical properties of wood by heat-exposure [6,8], the underlying modes of action remain a

subject for research.

Mechanical behavior of heat-treated wood is often determined in quasi-static three-point bending [7,12–14]. Stresses developed in three-point bending are a combination of compression stresses in the material at the top of the sample and tensile stresses in the material at the opposite region, while shear stresses develop in the neutral zone, where bending stresses become zero. When testing small clear samples of unmodified wood, the tensile strength usually exceeds the compression strength, thus bending is governed by compression behavior with pronounced inelastic deformation [15]. The effect of HT on the bending behavior of wood is most noticeable as a loss in strain energy (area below the stress-strain curve) caused by a reduction in strength and ductility, while the stiffness remains almost unchanged. The extent of this change in the mechanical behavior is dependent on the treatment temperature and duration applied [7,9,14], and is predominantly caused by the chemical changes occurring in the wood cell wall during HT [9].

There is a complex link between the chemical composition as well as the ultra-structural arrangement of the cell wall and the mechanical behavior of wood under various loads [16–18]. When an external load is applied, the cell wall polymers contribute in different degrees to the

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strength, stiffness and ductility of the wood. Cellulose microfibrils act as tensile reinforcements. They exhibit an extremely high modulus of elasticity (MOE) under tension and contribute greatly to the stiffness of the cell wall [19]. Under compression, however, cellulose microfibrils buckle easily [20]. This low resistance against compression loads is compensated by the cell wall matrix that contains a rigid lignin network [20–22]. Lignin also limits the access of water to the cell wall, enabling it to retain its strength and stiffness in humid environments [23,24]. However, lignin is not bonded to the cellulose directly, thus hemicelluloses are required as coupling agents that enable the transfer of stresses between the individual polymers, so that the cell wall acts as a continuum. Although hemicelluloses are presumably not bonded to the cellulose microfibrils covalently either, hydrogen bonds between these polymers are formed, which is further supported by physical entanglement within the non-crystalline regions of the microfibrils [17,25,26]. Hemicelluloses are covalently bonded to the lignin by ester, ether and glycosidic bonds to form lignin carbohydrate complexes (LCC) that are difficult to separate [25].

During exposure of wood to elevated temperatures by HT, many chemical reactions of the cell wall polymers take place, which result in a deviation from the chemical composition and ultra-structural arrangement of untreated wood. Amorphous hemicelluloses are much more sensitive to thermal degradation than the semi-crystalline cellulose or the lignin [27]. Hemicelluloses are hydrolyzed, resulting in shorter polymer chains, and subsequent dehydration leads to the formation of furan-type intermediates, such as furfural and hydroxyl methyl furfural (HMF) derived from pentoses and hexoses, respectively [28,29]. Furfural and HMF become volatile at elevated temperatures and are released from the wood to cause a mass loss (ML) [30].

The change in bending properties as a consequence of HT can often be described as a function of ML [31,32], which might be interpreted as evidence that the change in the mechanical behavior is pre-dominantly caused by the de-polymerization of hemicelluloses. Removing the hemicelluloses by HT is believed to affect the load sharing capability of the cell wall, thus internal stresses in wood caused by an external load are no longer distributed over the cell wall polymers as a continuum [6]. As recently reviewed by Winandy [8], a vast number of studies on the effects of elevated temperature, chemical treatments or biological decay point towards a singular relationship between strength loss and a uniform degradation sequence of the cell wall polymers, i.e. the hemicelluloses. Winandy [8] hypothesized that strength loss during heat-exposure proceeds in the order of: (1) hydrolytic de-polymerization of side-chain hemicelluloses, which is followed by (2) the hydrolytic de-polymerization of the main-chain hemicelluloses, and finally, at high strength loss levels by (3) the de-polymerization of cellulose and/or lignin.

However, this hypothesis does not consider the many re-polymerization reactions and ultra-structural rearrangements that occur in addition to the de-polymerization of the cell wall polymers [33]. During HT of wood, re-polymerization by ester bond formation [34,35], or by condensation reactions involving lignin and furan-type intermediates derived from hemicelluloses degradation [33,36,37], are likely pathways for modification of the cell wall matrix ultra-structure. Such covalent bond formation by re-polymerization is likely to affect the mechanical performance of heat-treated wood. Unfortunately, this effect is often overlooked, because it is difficult to separate the effects of cell wall polymer de- and re-polymerization during HT, as they are interrelated and occur simultaneously.

We hypothesized that re-polymerization reactions contribute significantly to the decrease in strength and ductility by HT. To test this hypothesis we compared the effect of HT of wood in dry state at high temperatures (180–240 °C) in a superheated steam atmosphere with HT of wood in wet state at mild temperatures (120–170 °C) in pressurized hot water. By variation of the treatment temperature for both HT techniques, we aimed at a wide range of thermal degradation intensities, which was quantified by ML. We speculated that the HT of

wood in wet state favors de-polymerization over re-polymerization reactions compared to HT of dry wood at high temperatures. We analyzed this shift in de- and re-polymerization reactions by FT-IR spectroscopy and the analysis of the chemical composition and compared its impact on the change in the mechanical performance under quasi-static load. Since the treatment conditions applied differed significantly between the HT techniques, the results were analyzed as a function of ML.

2. Material and methods

2.1. Material

Kiln-dried boards of Scots pine (*Pinus sylvestris* L.) wood were used for all experiments. For bending tests, samples with dimensions of $13 \times 13 \times 180 \text{ mm}^3$ ($r \times t \times l$) with 15 replicates per variety (treatment process, peak temperature) were heat treated, while for compression tests samples with dimensions of $23 \times 23 \times 110 \text{ mm}^3$ ($r \times t \times l$) with six replicates per variety were treated. The samples were clear of heartwood, knots and visible defects. All samples were oven-dried prior to HT using a temperature sequence of 40, 60, 80 and finally 103 °C, with each temperature held for ca. 24 h, before the determination of initial dry mass.

2.2. Heat treatments

Wet heat-treatment (HT_{wet}): The samples were vacuum-impregnated (ca. 50 mbar for 1 h) with deionized water 24 h before HT_{wet} . HT_{wet} was conducted in an air bath digester, which held several autoclaves (2.5 l volume) that were heated in hot air while rotating slowly. The samples were placed in the autoclaves together with deionized water in a solid to liquid ratio of 1:20 (g/g). The water temperature was increased fast until reaching 80 °C and then at a constant rate of 55 °C h^{-1} until reaching the respective peak temperature: 120, 130, 140, 150, 160 or 170 °C. After a 120 min. holding stage at the respective peak temperature, the vessels were removed from the hot air bath and placed in a cold water bath for 30 min under continuous water flow. Finally, any remaining pressure was released via a needle valve and the samples were removed from the vessels.

Dry heat-treatment (HT_{dry}): The samples were kept in dry state in a desiccator with silica gel until HT_{dry} . HT_{dry} was performed in an oven with continuous insertion of superheated steam. An initial temperature of 105 °C was applied for 30 min and then the temperature was increased stepwise by 15 °C every 30 min until reaching the respective peak temperature: 180, 195, 210, 225 or 240 °C, which was held for 180 min. After that, the oven heating was switched off and the temperature decreased to < 100 °C within one hour, after which the samples were removed from the oven.

All samples, including the reference samples, were leached with deionized water after the treatment. Dry heat-treated and reference samples were vacuum-impregnated with deionized water before leaching. Within the course of two weeks, the water was changed daily, before the samples were dried carefully at ambient conditions for a minimum of one week and then in an oven by applying the temperature sequence described above. Besides removal of remaining, water-soluble degradation products, the water-leaching caused maximum swelling of the samples to remove any reversible, drying related-effects [13,38]. The mass loss caused by treatment and leaching, ML (%), was calculated based on the dry mass of each sample before and after the process.

2.3. Chemical composition

Samples tested in three-point bending (2.5) were milled and mixed in a Wiley mill to pass through a 30 mesh screen. 6 g of wood particles were extracted in a Soxhlet apparatus with acetone for 6 h. Determination of carbohydrates and lignin was performed on the extracted samples according to the analytical procedure (NREL/TP-510-

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