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Differences in the mechanical behaviour of wood after thermal modification in oven-dry or water-saturated state

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ABSTRACT

The loss in strength and ductility of wood during the thermal modification is a major drawback that hinders its use in load-bearing applications. Up until today, the link between the chemical changes during the thermal modification and the changes in the mechanical behaviour is still not fully understood. This study aims at separating the effect of depolymerisation of cell wall polymers (i.e. hemicelluloses) and the effect of the formation of additional cross-links in wood during the thermal modification process on its mechanical behaviour. This is achieved by comparing the thermal modification of water-saturated wood in pressurized hot water at mild temperatures (≤170 °C) with the thermal modification of oven-dry wood in a superheated steam atmosphere at elevated temperatures (≥180 °C). Analysis of the chemical composition evidenced that both modification processes caused the preferential removal of hemicelluloses. However, additional repolymerisation reactions during the modification of dry wood caused an overestimation of the lignin percentage and an underestimation of the hemicellulose percentage based on the obtained mass loss. In contrast, the partial depolymerisation of lignin resulted in the overestimation of the hemicelluloses percentage based on the mass obtained by the modification of wood in water-saturated state. The bending strength and strain energy density of wet thermally modified wood decreased along the depolymerisation sequence that was reported previously. This verifies the role of hemicelluloses as coupling agents for the transfer of stresses over the cell wall as a continuum. However, a higher lignin percentage and enhanced cross-linking in dry thermally modified wood resulted in an additional reduction in strength, strain energy density and ductility. This was assigned to the prevention of inelastic deformation during bending that hindered compression yielding and caused a brittle tension failure in the dry modified wood. The results suggest the role of hemicellulose depolymerisation in causing a brittle failure in bending to be smaller than suggested previously.

INTRODUCTION

Thermal modification is applied on industrial-scale for more than two decades to prolong the service life of wood by increasing its dimensional stability and biological durability. However, this property change induced by cell wall changes during the exposure to heat is accompanied by a loss in strength and ductility (Kuboijima et al. 2000; Boonstra et al. 2000).
The latter may cause problems in load-bearing applications. Mechanical behaviour of thermally modified wood is often determined in quasi-static three-point bending tests. During such tests, compression stresses develop at the top of the sample and tensile stresses in the material at the opposite region, while shear stresses occur in the neutral zone, where the bending stresses become zero. For small and defect-free samples of unmodified wood, the tensile strength usually exceeds the compression strength, which results in distinct compression yielding with pronounced inelastic deformation during bending (Buchanan 1990). Besides reducing the bending strength, thermal modification results in a large loss in strain energy (area below the stress-strain curve), while the stiffness remains almost unchanged. The magnitude of these changes are strongly dependent on the modification temperature and duration applied and are linked to chemical changes in the wood cell wall (Boonstra et al. 2007).

During thermal modification, amorphous hemicelluloses are preferentially degraded, resulting in the increase in the content of crystalline cellulose and lignin in the wood residue (Kollmann and Fengel 1965). Hemicelluloses are expected to act as coupling agents that enable the transfer of stresses over the cell wall as a continuum. Thus, their preferential removal is assumed to be the major factor in reducing the strength and toughness of thermally modified wood (Hughes et al. 2015; Winandy 2017). Winandy (2017) hypothesized that the loss in strength loss during heat-exposure proceeds in the order of: (1) hydrolytic depolymerisation of side-chain hemicelluloses, which is followed by (2) the hydrolytic depolymerisation of the main chain hemicelluloses, and only at high strength loss levels by (3) the depolymerisation of cellulose and/or lignin. Although this depolymerisation sequence is not only applicable to the strength loss caused by heat-exposure, but also to the loss in strength by chemical treatments or biological decay (Winandy 2017), it does not consider the contribution of repolymerisation reactions to the change in mechanical behaviour. During the thermal modification of wood, repolymerisation reactions may lead to additional covalent bonds and cross-links in the cell wall matrix of the modified wood. Ester bond formation (Tjeerdsma and Militz 2005; Liang and Wang 2017) or condensation reactions between the lignin and furan-type derivatives derived from the degradation of hemicelluloses (Inari et al. 2007), are likely pathways for such enhanced cross-linking. These repolymerisation reactions are likely to affect the mechanical behaviour of thermally modified wood in addition to the effect of depolymerisation of cell wall polymers. However, this effect is often overlooked, because de- and repolymerisation reactions are interrelated and occur simultaneously, thereby hindering the separation of their individual impact.

This study attempts to separate the effect of de- and repolymerisation reactions during thermal modification on the mechanical behaviour of Scots pine (Pinus sylvestris L.) sapwood by applying two different modification methods to the wood. Thermal modification of oven-dry wood at temperatures between 180 and 240 °C in superheated steam at atmospheric pressure was applied to facilitate cross-linking within the cell wall matrix. In contrast, thermal modification of water-saturated wood in pressurized hot water at temperatures between 120 and 170 °C was applied to favour hydrolytic depolymerisation of cell wall polymers. The mechanical behaviour of the modified wood was evaluated by testing three-point bending and compression parallel to the grain. Analysis of the chemical composition was performed on the same material.
EXPERIMENTAL

Material
Kiln-dried boards of Scots pine sapwood were cut to samples with dimensions of 13×13×180 mm$^3$ (R×T×L) and 23×23×110 mm$^3$ (R×T×L). All samples were free of heartwood, knots and visible defects. All samples were oven-dried using a temperature sequence of 40, 60, 80 and finally 103°C, with each temperature being held for ca. 24 h, for the determination of the initial dry mass.

Thermal modification processes
For the thermal modification in dry state ($\text{TM}_{\text{dry}}$) the samples were kept in a desiccator over silica gel until the treatment. $\text{TM}_{\text{dry}}$ was performed in an oven with continuous insertion of superheated steam by increasing the temperature stepwise by 15 °C every 30 min starting from an initial temperature of 105 °C until reaching the target maximum temperature. Treatments with maximum temperatures of 180, 195, 210, 225 and 240 °C were applied for 3 h and then the oven temperature was decreased to >100 °C.

For the thermal modification in wet state ($\text{TM}_{\text{wet}}$), the samples were vacuum-impregnated (50 mbar for 1 h) with deionized water approx. 24 h before the treatment. The samples were placed in closed vessels with a volume of 2.5 l together with deionized water in a solid to liquid ratio of 1:20 (g/g). The vessels were heated to the maximum temperature at a rate of ca. 55 °C h$^{-1}$ in an air bath digester while rotating slowly. Treatments with maximum temperatures of 120, 130, 140, 150, 160 and 170 °C were applied for 2 h, before the vessels were removed from the air bath digester and placed in a cold water bath under continuous water flow for 30 min.After the thermal modification processes, all samples were leached with deionized water for 14 days with daily water changes. Reference samples and samples treated by $\text{TM}_{\text{dry}}$ were vacuum impregnated with deionized water prior to the water leaching. After the leaching, the samples were oven-dried by applying the temperature sequence described above to determine the final dry mass and calculate the mass loss (in %) caused by thermal modification.

Chemical composition
Samples tested in three-point bending were milled in a Wiley mill to pass through a 30 mesh screen and extracted in a Soxhlet apparatus with acetone. Determination of carbohydrates and lignin was performed according to the analytical protocol NREL/TP-510-42618 (Sluiter et al. 2012). Carbohydrates were determined by High Performance Anion Exchange Chromatography with Pulse Amperometric Detection (HPAEC-PAD) in a Dionex ICS-3000 column. The acid-soluble lignin was determined in a Shimadzu UV-2550 spectrophotometer using a wavelength of 205 nm and an absorptivity constant of 110 L g$^{-1}$ cm$^{-1}$. The acid-insoluble fraction was determined gravimetrically after drying at 103 °C for 12 h. The lignin percentage was calculated as the sum of the acid-soluble and the acid-insoluble fraction. Hemicellulose percentage was calculated as the sum of all detected monosaccharides except glucose. All samples were analysed in duplicate. The results are given as ratios with the value of the unmodified reference set to 1.

Mechanical testing
All samples with initial dimensions of 13×13×180 mm$^3$ and 23×23×110 mm$^3$ were conditioned at 20°C and 65% RH and then processed to samples with dimensions of 10×10×180 mm$^3$ (for bending tests) and 20×20×30 mm$^3$ (for compression tests), respectively. The bending test was conducted with 15 replicates per sample group (treatment process and maximum temperature) on a universal testing machine (Zwick
1475) equipped with a 20 kN load cell and combined with a MTS Premium Elite controller. The span length was set to 150 mm and the load was applied in the tangential direction at a rate of 3 mm min\(^{-1}\). Deflection (δ, in mm) was set to zero at a load (P, in N) of ca. 4 N. Bending strength (MOR, in N mm\(^{-2}\)) was defined as the maximum stress. Modulus of elasticity (MOE, in N mm\(^{-2}\)) was determined as the slope of a linear regression curve of the stress-strain curve within the range between 10 and 40 % of MOR. Strain energy density (u, in kJ mm\(^{-3}\)) was computed as the area below the stress-strain curve up to the strain at maximum stress (\(\varepsilon_{\text{max}}\), in mm mm\(^{-1}\)). Elastic strain (\(\varepsilon_{\text{elastic}}\)) and elastic strain energy density (u\(_{\text{elastic}}\)) were calculated according to Eqn. 1 and Eqn 2.

\[
\varepsilon_{\text{elastic}}=\frac{\text{MOR}}{\text{MOE}} \tag{1}
\]
\[
\text{u}_{\text{elastic}}=\text{MOR} \times \left(\frac{\varepsilon_{\text{elastic}}}{2}\right) \tag{2}
\]

Brittleness was quantified by the brittleness index (BI, in %) that was calculated based on Eqn. 3.

\[
\text{BI}=100 \times \left(\frac{\text{u}_{\text{elastic}}}{\text{u}}\right) \tag{3}
\]

The compression test parallel to the grain was conducted with 18 replicates per sample group on the same universal testing machine, but with a 100 kN load cell. The load was applied in the longitudinal direction at a rate of 1 mm min\(^{-1}\). Displacement (in mm) was set to zero at a load (P, in N) of ca. 30 N. Maximum stress was defined as compression strength (CS, in N mm\(^{-2}\)).

The specific gravity (in kg mm\(^{-3}\)) of all samples was determined by relating the volume in conditioned state to the respective dry mass. By dividing MOR, u and CS by the specific gravity, the specific MOR (\(\text{MOR}_{\text{spec}}\), in N mm kg\(^{-1}\)), the specific strain energy density (\(\text{u}_{\text{spec}}\) in kJ kg\(^{-1}\)) and the specific CS (\(\text{CS}_{\text{spec}}\), in N mm kg\(^{-1}\)) were computed for each sample. \(\text{MOR}_{\text{spec}}\), \(\text{u}_{\text{spec}}\) and \(\text{CS}_{\text{spec}}\) are given as ratios with the value of the unmodified reference set to 1.

**Scanning electron microscopy**

Samples treated by TM\(_{\text{dry}}\) at 240 °C and samples treated by TM\(_{\text{wet}}\) at 170 °C, with bending properties close the group average were selected for the investigation of the fracture surface by scanning electron microscopy (SEM). Small cross-cuts with a length of ca. 40 mm were taken from the bending samples for SEM observations. The samples were dried at 50 °C and <100 mbar for 24 h and sputter-coated with gold-palladium, before the observation in a Zeiss Sigma VP SEM (Oberkochen, Germany). The observation was limited to the tension side of the fracture surface.

**RESULTS AND DISCUSSION**

**Chemical changes**

Both modification techniques resulted in the preferential removal of hemicelluloses and an accumulation of lignin and cellulose in the wood residue. The presence of excessive amounts of water during TM\(_{\text{wet}}\) caused a very efficient removal of wood mass, which lead to a larger mass loss by TM\(_{\text{wet}}\) at 170 °C for 2 h (25.2 %) than by TM\(_{\text{dry}}\) at 240 °C for 3 h (14.1 %). This is caused by the catalytic effect of hydronium ions formed by water auto-ionization, and the formation of acetic acid that accumulates in the process water during TM\(_{\text{wet}}\) (Garrote et al. 1999). However, there are differences in the compositional changes
as a function of mass loss, which are a consequence of the shift from the preferential hydrolytic depolymerisation during TM \( \text{wet} \) to additional repolymerisation during TM \( \text{dry} \). Figure 1 shows the lignin and hemicellulose ratios as a function of the mass loss caused by the modification process. The increase in lignin by TM \( \text{wet} \) is lower than calculated when assuming that mass loss is solely caused by carbohydrate removal, which evidences a partial depolymerisation and removal of lignin. In contrast, the increase in lignin by TM \( \text{dry} \) is larger than calculated. Furan-type derivatives (i.e. furfural and HMF) are formed by the dehydration of hydrolysed hemicelluloses. Repolymerisation reactions that involve such degradation products and the lignin add to lignin percentage that is determined using the analytical protocol applied (Inari et al. 2007). Such repolymerisation is also one potential pathway for the creation of additional cross-links within the cell wall matrix of dry thermally modified wood.

Differences in the extent of de- and repolymerisation reactions also affect the decrease in hemicellulose ratio (Figure 1 B). The degradation of hemicelluloses is overestimated based on the mass loss in case of TM \( \text{wet} \), because removal of lignin partially contributes to the mass loss. In contrast, mass loss underestimates the degradation of hemicelluloses during TM \( \text{dry} \), because the hemicellulose degradation products partially remain within the wood due to their involvement in repolymerisation reactions. However, the analysis of the different monosaccharides found in the wood hydrolysates (data not shown) evidenced the same temperature-dependent depolymerisation sequence for both modification processes: monosaccharides found primarily at the side chains (arabinose and galactose) were removed more rapidly during thermal modification than monosaccharides that built the main chain of the hemicelluloses (mannose and xylose).

**Mechanical properties**

Thermal modification decreases the density of the wood, thus stresses are distributed over less cell wall material. This density effect was removed from the data by analysing specific values that are related to the respective specific gravity of each sample. Changes of these specific values can be directly assigned to changes in chemical composition and in the structural arrangement of the cell walls.

Since the MOEspec ratio remained nearly constant, except for a small decrease to 0.87 at after TM \( \text{wet} \) at 170 °C, the data is excluded from the analysis. Figure 2 shows the changes in MORspec, uspec and BI as a function of the hemicellulose ratio. If the depolymerisation of hemicelluloses during the thermal modification was the only factor that determines the
change in mechanical behaviour, no differences between TM\textsubscript{wet} and TM\textsubscript{dry} would be expected. However, the two modification processes differed strongly in their impact on the mechanical behaviour of the wood. After TM\textsubscript{wet}, MOR\textsubscript{spec} and u\textsubscript{spec} decreased linearly with decrease hemicellulose ratio, in line with the presumed impact of hemicellulose depolymerisation on the strength and toughness of wood (Hughes et al. 2015; Winandy 2017). Remarkably, the effect of TM\textsubscript{dry} on MOR\textsubscript{spec} and u\textsubscript{spec} as a function of the hemicellulose ratio was much stronger than the effect of TM\textsubscript{wet}. Especially in case of u\textsubscript{spec}, the decrease became non-linear, which indicates that the depolymerisation of hemicelluloses was not the only cause for the change in mechanical behaviour by TM\textsubscript{dry}.

The difference in the mechanical behaviour between the two modification processes was most noticeable for the BI. TM\textsubscript{wet} resulted in a slight increase in BI with decreasing hemicellulose ratio to a maximum of 55 %. Even for hemicellulose ratios as low as 0.78, the BI almost remained compared to the reference value of 41 %. However, at the same hemicellulose ratio, a BI above 80 % was reached by TM\textsubscript{dry} and a BI of 95 % was determined after TM\textsubscript{dry} at 240 °C, which demonstrates that the material failed almost without any inelastic deformation.

![Figure 2: Results of the three-point bending test in dependence on the hemicellulose ratio. (A) Specific bending strength ratio, (B) specific strain energy density ratio and (C) brittleness index (in %; C). The dotted line in (C) represents the average BI of the reference samples. (±95 % confidence interval)](image)

![Figure 3: SEM images of the fracture surface of the bending test samples taken on the tension side. (A) TM\textsubscript{dry} at 240 °C; (B) TM\textsubscript{wet} at 170 °C. (Scale bar = 30 µm)](image)
The differences in the mechanical behaviour were also clearly visible in the SEM observation of the fracture surfaces (tension side) of selected bending samples (Figure 3). After TM\textsubscript{dry} at 240°C, the fracture surface was very flat and the cell wall appeared as if cut by a razor blade. Such a fracture is typical for the brittle failure of dry thermally modified wood (Boonstra et al. 2007). In contrast, a more ragged fracture surface with fibril structures sticking up from the cell wall was observed after TM\textsubscript{wet} at 170°C.

The differences in the bending test results between the two modification processes can be explained by an additional restriction in inelastic deformation of the dry modified wood compared to the wet modified wood. A loss in inelastic deformation leads only to a small loss in strength, because the increase in stress as a function of strain is comparably low in the inelastic region. However, a loss in inelastic deformation causes a large reduction in strain energy density and ductility, in line with the differences between TM\textsubscript{wet} and TM\textsubscript{dry} shown in Figure 2. Inelastic deformation requires the rearrangement of the cell wall polymers by plastic flow. This might be partly reduced by a higher percentage of lignin, which forms a rigid network in the cell wall, in dry compared to wet modified wood. However, strong differences in the bending behaviour are already evident at mild modification intensities, where differences in the lignin percentage are comparably low.

As discussed in detail in previous studies (Altgen et al. 2016, 2018), TM\textsubscript{dry} also results in a more facile formation of cross-links within the cell wall than TM\textsubscript{wet}, which are likely to further reduce the inelastic deformation under bending loads.

![Figure 4: Specific compression strength in dependence on the mass loss. (±95 % confidence interval)](image)

In unmodified wood, the inelastic deformation originates mostly from compression yielding at the top of the sample (Buchanan 1990). In line with the conclusion of a hindered inelastic deformation in bending by additional cross-linking, TM\textsubscript{dry} increased the CS\textsubscript{spec} ratio with increasing mass loss (Figure 4), which prevents compression yielding during bending to cause a brittle tension failure. In contrast, the CS\textsubscript{spec} ratio decreased by TM\textsubscript{wet}, thereby enabling inelastic deformation by compression yielding even at large levels of hemicellulose depolymerisation.

**CONCLUSIONS**

The strength and strain energy density of wood that was thermally modified in watersaturated state at mild temperatures (≤170°C) in pressurized hot water, decreased along the depolymerisation sequence reported previously. However, thermal modification of dry wood at elevated temperatures (≥180°C) in superheated steam resulted in an additional reduction in strength and strain energy density, which was assigned to the effect
of cross-links within the wood cell wall matrix that are formed during the modification of dry wood. Additional cross-links in the cell wall matrix of dry thermally modified wood hindered the compression yielding to cause a brittle tension failure during bending. The lack of cross-linking during the thermal modification in water-saturated state enabled inelastic deformation by compression yielding even at high levels of hemicellulose removal.

REFERENCES


