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## **Polymers & biopolymers**



# Micro-tensile behavior of Scots pine sapwood after heat treatments in superheated steam or pressurized hot water

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## ABSTRACT

Heat treatments reduce the strength and ductility of wood, but the extent depends on the direction of load and the treatment conditions applied. The tensile behavior of wood is very sensitive to heat treatments, but there is a lack of understanding how this is related to different heat treatment conditions. In this study, we treated homogeneous micro-veneers under different time-, temperature-, and moisture-environments and compared the effect on the tensile behavior of the treated veneers based on their chemical composition changes. The results confirmed the adverse effect of the preferential hemicellulose removal on the strength and toughness of wood. However, chemical composition changes could not fully explain the tensile behavior of dry heat-treated wood, which showed an additional loss in maximum load and work in traction at the same residual hemicellulose content compared to wet heat-treated wood. The scission of cellulose chains as well as the enhanced cross-linking of the cell wall matrix under dry heat conditions and elevated temperatures was discussed as additional factors. The enhanced cross-linking of the cell wall matrix helped in preserving the tensile properties when testing the veneers in water-saturated state, but may have also promoted the formation of cracks that propagated across the cell wall during tensile loading.

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## **GRAPHIC ABSTRACT**



## Introduction

Heat treatments (HTs) are applied commercially using a variety of process techniques that aim at prolonging the service life of wood in exterior applications by improving its dimensional stability and decay resistance [1]. The change in wood properties by HT is based on the partial thermal degradation of wood, which also results in a decrease in strength and ductility [2, 3]. The effect of HT on the strength of wood depends on the direction of the load. Typically, the loss in tensile strength of heattreated wood exceeds the loss in compression or bending strength [2]. However, while there are a number of studies that relate chemical changes during HT to changes in the performance of wood under bending or compression loads [3-6], there is a lack of research on the tensile behavior of heat-treated wood and its dependence on the treatment conditions.

The main structural elements in softwood species are tracheids, which are long and hollow cells with a length of 2–4 mm and a diameter of 20–50  $\mu$ m [7, 8]. Their cell walls are composites made of cellulose, hemicelluloses and lignin and their structural arrangement determines the mechanical performance of wood [9, 10]. The behavior of wood under tensile loads parallel to the fiber direction is highly dependent on the cellulose within the wood cell wall, which contributes to 40-50% of the wood dry mass and has an elastic longitudinal modulus of about 140–150 GPa [9, 10]. Cellulose chains are aggregated into semi-crystalline microfibrils and bundles thereof, which are embedded in an intimately mixed matrix of amorphous hemicelluloses and lignin [11]. The cellulose microfibrils circulate helically around the longitudinal cell axis, and there are different inclinations of the parallel-oriented microfibrils with respect to the cell axis (microfibril angle, MFA) [12]. In the thickest S<sub>2</sub> cell wall layer, which accounts for more than 80% of the fiber wall by weight, the MFA is very small [10] and this low MFA in the  $S_2$  layer provides the wood with a high tensile strength parallel to the fiber direction.

Despite the dominant role of the cellulose as loadbearing polymer under tensile loads along the fiber direction [13, 14], the tensile behavior of wood is also influenced by the cell wall matrix polymers that surround the cellulose microfibrils [13, 15–19]. Lignin is not coupled to the load-bearing cellulose directly and a molecular deformation of lignin is only recorded when the wood fibers are highly deformed [17]. Lignin is believed to have a more indirect role in the transfer of tensile stresses across the untreated cell wall. In particular, lignin helps the wood to preserve its strength under wet conditions [18]. Removal of lignin does not decrease the tensile strength of wood when tested under dry conditions, but increases the pliability and the elongation at fracture [16, 18].

In contrast to lignin, hemicelluloses are directly involved in the transfer of tensile stresses. A mechanical interaction with cellulose under tensile loads parallel to the grain has been reported for glucomannan in spruce wood [13]. Hemicelluloses bind to cellulose and to lignin [20, 21], and could act as coupling agents between the cellulose and the cell wall matrix, or between adjacent cellulose microfibril bundles [22, 23]. The role of hemicelluloses as coupling agents for the transfer of stresses within the cell wall is in line with strength loss of wood by thermal degradation. Significant loss in strength by HT can be measured even when no degradation of cellulose occurred. Instead, initial strength loss by thermal degradation is primarily assigned to the degradation of hemicelluloses, which are less temperature stable than cellulose or lignin. Loss in hemicelluloses is believed to interfere with the load-sharing capabilities of the cell wall, which prevents the remaining cell wall polymers to act as a continuum when an external load is applied [24, 25].

Recently, this theory was extended by an additional mechanism in heat-treated wood [6]. It was shown that the heat treatment of wood in dry state resulted in an additional loss in strength and toughness under bending loads compared to wood that was heat-treated in water-saturated state. This could not be assigned to differences in mass loss or chemical composition. Instead, this was explained by the enhanced crosslinking within the residual cell wall matrix in dry heattreated wood, which did not occur when the wood was heat-treated in wet state. The authors suggested that the enhanced cross-linking prevented the inelastic deformation of wood by compression yielding to cause a brittle failure in a three-point bending test [6]. However, it remained unclear if the tensile behavior of heat-treated wood shows the same dependence on the applied HT conditions. A recent study on heat-treated Japanese red pine (Pinus densiflora) showed indeed that the tensile behavior was not only determined by the resulting loss in wood mass, but was also affected by the conditions (temperature and duration) applied to reach a given mass loss [19].

Using a similar approach as in a previous experiment [6], this study investigated the tensile behavior of wood that was heat-treated in dry state using superheated steam at atmospheric pressure, or in wet state using pressurized hot water. To minimize raw material based variation, the tensile tests were conducted on thin micro-veneers that originated from the same wood blocks. Thereby, the tensile behavior could be directly related to chemical composition changes caused by the heat treatments. If the tensile behavior of heat-treated wood was solely determined by the loss in hemicelluloses, a linear correlation between tensile properties and hemicelluloses content would be expected, independent of the applied HT conditions.

#### Materials and methods

## **Preparation of micro-veneers**

A total of six blocks of Scots pine (Pinus sylvestris L.) with dimensions of  $15 \times 40 \times 30 \text{ mm}^3$  (tangential × radial × longitudinal) were prepared from a single slat (Fig. 1). The annual ring orientation deviated by ca. 10° from the radial plane to avoid stretching of wood rays over the micro-veneer surface. The blocks were vacuum-impregnated with 10% aqueous ethanol at ca. 50 mbar for 2 h and left to soak in fresh aqueous ethanol for 3 days. Micro-veneers with a thickness of 60 µm were cut from the soaked blocks using a rotary microtome. The wet micro-veneers were fixed between two glass slides in bundles of forty and stored at 20 °C and 65% RH until HT. The thickness of each veneer was measured on a micrometer (SE250, Lorentzen & Wettre, Sweden) and veneers that deviated from the average thickness by more than 15% were discarded.

#### Heat treatments

Two different HT techniques were applied and the treatment conditions were chosen based on previous studies to ensure that the resulting decrease in hemicelluloses content was in a similar range [6, 26]. For treatments in superheated steam at atmospheric pressure (Dry-HT), the micro-veneers were fixed between two stainless steel plates and placed into a steam-oven that was pre-heated to 105 °C. The temperature in the oven was increased by 15 °C every 30 min until reaching a treatment temperature of 210 °C, which was held for 1, 3, 5 or 7 h, before the oven heating was switched off to decrease the temperature below 100 °C within 1 h. Steam was continuously inserted into the oven throughout the

Figure 1 Preparation of micro-veneers from axially matched wood blocks and testing of the veneers by finitespan micro-tensile testing parallel to the fiber direction.



treatment while atmospheric pressure maintained. For treatments in pressurized hot water (Wet-HT), the micro-veneers were soaked in deionized water overnight and filled into small stainless steel vessels together with 200 ml of deionized water. The vessels were closed tightly and heated in an oil bath at 140 °C for 1, 3, 5 or 7 h, before cooling in cold tap water for ca. 10 min.

After the treatments, all samples were stored in deionized water for a minimum of 3 days. A total of 24 veneers per sample group (four veneers per block) was kept in deionized water at 25 °C with regular water changes for a maximum of 2 weeks until micro-tensile testing. Another set of 24 veneers per sample group was fixed between two glass slides and dried at 60 °C for ca. 24 h, before conditioning at 23 °C and 50% RH for a minimum of 2 weeks until the micro-tensile testing. For samples that were treated in pressurized hot water, another set of 24 veneers per sample group was first dried at 60 °C for 24 h, which was followed by soaking in deionized water at 25 °C for a minimum of 48 h before the micro-tensile testing ("rewet"). Veneers with visible defects due to handling of the heat-treated veneers were discarded prior to micro-tensile testing, leading to small deviations in the number of veneers that were tested for each sample group.

#### Micro-tensile testing

The tensile tests were performed on a MTS 400/M tensile tester (MTS Systems Corporation) using a 200 N load cell. The distance between the two clamps was set to 25 mm (Fig. 1). Preliminary tests with clamping forces between 0.15 and 0.3 MPa showed the highest average maximum load at a force of 0.25 MPa. This clamping force was considered as the

optimal compromise between slippage of the veneers at low clamping forces and crushing of the veneers at high clamping forces and was applied during the actual test series. The veneers were tested at a speed of 1 mm min<sup>-1</sup> and elongation was set to zero and at a pre-load of ca. 3 N. The work in traction was determined by integration of the load-elongation curve until maximum load. The stiffness was calculated as the slope of the load-deformation curve between 10 and 40% of the maximum load. The tensile properties of the treated veneers were calculated as residual stiffness, residual maximum load and residual work in traction by relating the stiffness, maximum load or work in traction of the treated samples to the corresponding average value of the reference samples that were measured in the same moisture state (conditioned or water-saturated).

#### Chemical composition analysis

Micro-veneers were milled in a Wiley mill to pass through a 30 mesh screen and extracted in a Soxhlet apparatus with acetone for 6 h. Lignin and carbohydrates were determined by acid hydrolysis according to NREL/TP-510-42618 [27], as described previously [6]. The ash content was determined according to TAPPI 211 on-02 by exposing oven-dried samples to 525 °C for 5 h. The chemical composition was calculated on an extractive-free, oven-dry basis. The lignin content was calculated as the sum of the acid-soluble and insoluble fraction. The contents of cellulose, hemicelluloses, xylan and glucomannan were calculated according to Janson [28]. All measurements were done in duplicate.

## Infrared spectroscopy

Fourier transform infrared (FT-IR) spectra of wood micro-veneers were measured using a FT-IR spectrometer (Spectrum Two, PerkinElmer, USA) equipped with an ATR unit and a diamond crystal. Spectra were acquired within the wavenumber region 4000–750 cm<sup>-1</sup> at a resolution of 4 cm<sup>-1</sup> and 8 accumulations. The spectra were baseline corrected and normalized to the absorbance at 1509 cm<sup>-1</sup>.

## **Dynamic vapor sorption**

The water sorption behavior within the hygroscopic range (0-95% RH) was analyzed in a dynamic vapor sorption (DVS) apparatus (DVS intrinsic, Surface Measurement Systems, London, UK) at a temperature of 25 °C and a gas flow of 200 sccm. Approx. 15 mg of micro-veneers were placed on a sample pan and exposed to a dry nitrogen flow ( $\sim 0\%$  RH) to determine the dry mass of the sample. This was followed by the exposure to 50% and finally 95% RH. Each RH-step, including the drying step at 0% RH, was kept until the mass change per minute (dm/dt)was less than 0.0005% min<sup>-1</sup> over a 10 min period. The dm/dt was calculated using a 10 min regression window. The chosen dm/dt value was lower than the value recommended by the manufacturer for the used in this sample mass study (dm/dt 0.002% min<sup>-1</sup>) in order to reduce the deviation from the equilibrium state. The wood MC (in %) was quantified as the mass of water related to the dry mass of the wood. In addition, sorption rates (in  $\% \text{ mg}^{-1} \text{ min}^{-1}$ ) were calculated as described by Himmel and Mai [29].

## Scanning electron microscopy

After the tensile tests, fracture surfaces of selected micro-veneers were observed by scanning electron microscopy (SEM). Besides untreated veneers, only micro-veneers that were heat-treated for 7 h were analyzed. Small pieces from several veneers were glued to aluminum stubs using carbon tape with the fracture surface facing upwards. They were coated with gold–palladium and observed in a SEM (Zeiss Sigma VP, Zeiss, Germany) using a beam acceleration voltage of 2 kV and a detector for secondary electrons.

## Statistical analysis

Micro-tensile data were analyzed using Welch-ANOVA with Games-Howell post hoc analysis. For each tensile property and HT technique, data were separated into groups depending on the treatment duration and the moisture state during tensile testing. Normal distribution was assessed by the Shapiro–Wilk test (p > 0.05) and logarithmic (Log<sub>10</sub>) transformation was applied when necessary. Furthermore, linear correlations between residual tensile properties and chemical composition were evaluated by Pearson correlation coefficients that were calculated based average values.

## Results

## Chemical changes during heat treatment

Both HT techniques led to a loss of hemicelluloses and a consequent accumulation of cellulose and lignin (Table 1). However, Wet-HT resulted in a faster decrease in hemicelluloses content than Dry-HT, despite the lower treatment temperature applied during Wet-HT. After a treatment duration of 7 h, the initial hemicelluloses content of ca. 25% had decreased to 19 and 13% after Dry-HT and Wet-HT, respectively. The increase in cellulose and lignin content approximately followed the decrease in hemicelluloses content. Therefore, a faster increase in lignin and in cellulose content over time was recorded for Wet-HT. The difference in cellulose content between the HT techniques was large, which was in line with the differences in hemicelluloses content. The cellulose content of wet heat-treated wood reached up to 125% of the reference value, while the cellulose content of dry heat-treated wood did not exceed 110%. Differences in lignin content were smaller and the lignin content was nearly identical for both HT techniques after a treatment duration of 7 h. The HT techniques also differed in the removal of the two main hemicelluloses in Scots pine. Wet-HT was particularly effective in removing glucomannan and less than 50% of the initial glucomannan content remained after a treatment duration of 7 h, whereas ca. 88% still remained after Dry-HT. The decrease in xylan content over time was similar for both HT techniques, and ca. 66% of the initial xylan content remained after a treatment duration of 7 h.



Table 1Chemicalcomposition of the micro-veneers after the different HTprocesses

Treatment	LIG (%)	CEL (%)	HEM (%)	GLM (%)	XYL (%)
Ref	28.3 (100)	43.2 (100)	25.3 (100)	15.8 (100)	8.0 (100)
Dry-HT					
1 h	28.3 (100)	44.9 (104)	24.5 (97)	15.9 (100)	8.0 (100)
3 h	28.4 (100)	46.0 (106)	22.7 (90)	15.2 (96)	7.2 (90)
5 h	29.1 (103)	47.4 (110)	21.2 (84)	14.8 (94)	6.1 (76)
7 h	31.2 (110)	47.3 (108)	19.3 (77)	14.0 (88)	5.3 (66)
Wet-HT					
1 h	27.9 (99)	46.6 (108)	23.2 (92)	14.9 (94)	7.8 (97)
3 h	30.4 (108)	51.1 (118)	16.7 (66)	10.3 (65)	6.3 (79)
5 h	31.0 (109)	52.9 (122)	13.8 (55)	7.9 (50)	5.6 (70)
7 h	31.3 (111)	54.0 (125)	13.0 (52)	7.3 (46)	5.3 (66)

For each cell wall constituent, the changes in composition relative to the respective reference value (= 100) are shown in parentheses

LIG lignin, CEL cellulose, HEM all hemicelluloses, GLM glucomannan, XYL xylan

Figure 2 FT-IR spectra in the wavenumber range  $1850-750 \text{ cm}^{-1}$  with insets highlighting the wavenumber range  $1830-1480 \text{ cm}^{-1}$  for wet (a) and dry (b) heat-treated micro-veneers. All spectra were normalized to the absorbance at  $1509 \text{ cm}^{-1}$ .



Chemical changes during HT were further analyzed by FT-IR spectroscopy (Fig. 2). The assignments of the FT-IR bands in the wavenumber region 1850–750 cm<sup>-1</sup> are listed in Supplementary Table S.1. Both HT techniques showed losses in absorbance at bands that were assigned to adsorbed water (1369 and 1643 cm<sup>-1</sup>). Furthermore, bands assigned to C–H and C–O absorbance (i.e., at 1029, 1053, 1105 and 1158 cm<sup>-1</sup>) decreased compared to the lignin-related band at 1509 cm<sup>-1</sup> that was used for normalization of the spectra, which showed the preferential degradation of carbohydrates during HT. In line with the chemical composition analysis (Table 1), wet heattreated wood showed a decrease at 809 and 870 cm<sup>-1</sup> due to the removal of glucomannan, which was not observed to the same extent in dry heat-treated wood. However, the FT-IR spectra also revealed chemical changes that could not be derived from the chemical composition data. Wet-HT resulted in a stronger decrease at 1264 cm<sup>-1</sup> than Dry-HT, which indicated the hydrolytic cleavage of ether linkages in lignin. Such pronounced hydrolytic action during Wet-HT was also in line with losses in absorbance at 1730 and 1231 cm<sup>-1</sup>, which was caused by the cleavage of acetyl groups from the hemicelluloses. Dry-HT did not cause a decrease at these two bands, but a shift toward lower wavenumbers.

Treatment	50% target H	RH			95% target F	RH		
	Measured RH (%)	MC (%)	MC (% of Ref)	Sorption rate (% mg <sup><math>-1</math></sup> min <sup><math>-1</math></sup> )	Measured RH (%)	MC (%)	MC (% of Ref)	Sorption rate (% $mg^{-1}$ min <sup>-1</sup> )
Ref	50.5	8.1	100	0.37	94.6	24.6	100	0.33
Dry-HT								
1 h	50.6	7.6	94	0.98	94.7	20.6	84	0.32
3 h	50.6	7.5	93	1.1	94.5	19.4	79	0.50
5 h	50.5	6.9	85	0.98	94.7	17.8	72	0.38
7 h	50.1	6.8	84	0.34	94.5	17.4	70	0.17
Wet-HT								
1 h	50.5	7.9	98	0.44	94.6	23.7	96	0.28
3 h	50.4	7.4	91	0.37	94.6	23.2	94	0.23
5 h	50.4	7.1	87	0.36	94.6	22.8	92	0.23
7 h	50.4	7.0	87	0.40	94.6	22.8	93	0.20

Table 2 Moisture contents and sorption rates measured after conditioning at 50 and 95% RH in the DVS apparatus

Each RH step was hold until the sample mass change per minute maintained at  $\leq 0.0005\%$  min<sup>-1</sup>

#### Dynamic water vapor sorption

The MC of the micro-veneers was measured in a DVS apparatus after conditioning at 25 °C and two different RH levels, 50 and 95% (Table 2). Conditioning at 25 °C and 50% RH was very similar to the conditioning temperature and RH of the veneers before the micro-tensile measurements in conditioned state (23 °C and 50% RH). However, the DVS apparatus cannot maintain a stable RH close to 100%. Hence, the MC measured at 95% RH was not an estimate for the amount of water within the cell walls of the veneers during the micro-tensile tests in water-saturated sate. Instead, the DVS measurements provided information on differences in the effectiveness of HT in reducing the MC at intermediate and high RH.

The MC of the wood was reduced by both HT techniques, but their effectiveness in reducing the MC differed, particularly at 95% RH. Despite higher residual hemicelluloses contents in dry heat-treated wood, both HT techniques resulted in similar MCs at 50% RH when the same treatment duration was applied. The deviation in MC at the same treatment duration did not exceed 0.3%-points. However, Dry-HT was particularly efficient in reducing the MC at 95% RH. At this RH level, Dry-HT for 1 h already decreased the MC to ca. 84% of the reference MC, while the MC of wet heat-treated wood did not decrease below 92% even for a treatment duration of 7 h. Furthermore, Dry-HT increased the sorption rate

during the conditioning at 50% RH compared to the reference, whereas the sorption rate remained nearly unchanged for wet heat-treated wood. Fewer differences in the sorption rate were found during the conditioning at 95% RH. For both HT technologies, the longest treatment duration resulted in the lowest sorption rate.

#### **Micro-tensile properties**

There was a large difference in the tensile behavior of the reference micro-veneers between the tests in conditioned and in water-saturated state. Tensile stiffness, maximum load and work in tension were roughly twice as high when tested in conditioned state compared to the tests in water-saturated state. However, to assess the effect of HT, the tensile properties of the heat-treated veneers were related to the corresponding average value of the reference veneers that were measured in the same moisture state. Hence, the average values of the reference sample group were set to 100% for all tensile properties and both moisture states.

Figure 3 shows the pair-wise comparison of the residual tensile properties in water-saturated and conditioned state for each treatment duration. In case of Wet-HT, the results of the tests in water-saturated state were limited to the rewetted veneers, which were oven-dried after the treatment followed by resoaking in water. This is more comparable to the tensile tests of dry-heat-treated veneers in water-





**Figure 3** Micro-tensile properties (in % of Ref) in dependence on the treatment duration for tensile tests in conditioned or watersaturated state after Wet-HT (**a**–**c**) or Dry-HT (**d**–**f**). Bars with different letters display significant differences (p < 0.05) based on the post hoc test. Error bars represent the standard deviation. The average tensile properties of the reference samples in conditioned and water-saturated state (each set to 100%) are shown.

saturated state, which also required the soaking of dry veneers in water. In most cases, the treatment duration had a significant effect (p < 0.05) on the tensile properties, i.e., on the residual maximum load and work in traction. For Wet-HT, however, nearly identical residual tensile properties were determined in water-saturated and in conditioned state (Fig. 3ac). Significant differences (p < 0.05) were only found for a treatment duration of 1 h, at which the tensile tests in water-saturated state resulted in a larger residual stiffness, but a lower residual maximum load and a lower residual work in tension compared to the tests in conditioned state. Therefore, the change in micro-tensile behavior by Wet-HT was nearly unaffected by the moisture state during testing. In contrast, the residual tensile properties of dry heattreated wood were always higher when tested in

water-saturated state compared to the tests in conditioned state. For most treatment durations, these differences were statistically significant (p < 0.05; Fig. 3d-f). Hence, the change in tensile behavior of dry heat-treated veneers was not only dependent on the treatment duration, but also on the moisture state during testing. Figure 3 also shows that the stiffness decreased slightly or increased after the treatments, whereas the maximum load and the work in tension decreased to less than 45 and 20% of the corresponding reference value. However, it is not sensible to compare the effect of the two HT techniques on the basis of the treatment duration, because significantly different treatment conditions were applied. Instead, the tensile behavior of Dry-HT and Wet-HT is compared on the basis of the chemical composition changes.

Correlations between the residual tensile properties and the chemical composition are shown by the scatter matrixes in Supplementary Fig. S.1 and Fig. S.2 for the tensile tests in conditioned and watersaturated state, respectively. As a general trend, the residual maximum load and the residual work in traction decreased with decreasing hemicelluloses contents and increasing cellulose and lignin contents. However, except for correlations between the residual maximum load and residual work in traction and between cellulose and hemicelluloses contents, the correlations were not uniform but dependent on the HT technique. Accordingly, Pearson correlation coefficients, which indicate linear relationships, were higher when calculated separately for dry and wet heat-treated wood (Tables 3, 4). While linear correlations that included residual stiffness and/or lignin were often weak ( $0.25 \le r \le -0.97$ ), residual maximum load and residual work in traction were negacorrelated cellulose tivelv with the content  $(r \leq -0.94)$  and positively correlated with the hemicelluloses content ( $r \ge 0.80$ ). Separating the hemicelluloses in glucomannan and xylan did not improve the correlation coefficients. Overall, linear correlations between tensile properties and chemical composition were slightly better for wet heat-treated than for dry heat-treated wood.

In view of the proposed, dominant role of hemicellulose degradation on the initial strength loss of heat-treated wood [24, 25], the changes in microtensile properties are shown in detail as functions of the residual hemicelluloses content (Fig. 4). When tested in conditioned state, the residual stiffness, Table 3Pearson correlationcoefficients for tensileproperties and chemicalconstituents based on tensiletests of micro-veneers inconditioned state

Variable	Dry-HT			Wet-HT			
	Stiffness	Max. load	Work in traction	Stiffness	Max. load	Work in traction	
HEM	- 0.50	0.88	0.80	0.74	0.99	0.99	
GLM	- 0.43	0.78	0.68	0.77	0.99	0.99	
XYL	- 0.35	0.82	0.71	0.77	0.99	0.99	
CELL	0.61	- 0.98	- 0.94	- 0.65	- 0.98	- 0.99	
LIG	0.25	- 0.61	- 0.51	- 0.97	- 0.96	-0.80	
Variable	Dry-HT			Wet-HT <sup>a</sup>			
Variable	Dry-HT Stiffness	Max. load	Work in traction	Wet-HT <sup>a</sup> Stiffness	Max. load	Work in traction	
Variable	Dry-HT Stiffness - 0.80	Max. load	Work in traction	Wet-HT <sup>a</sup> Stiffness 0.63	Max. load	Work in traction 0.94	
Variable HEM GLM	Dry-HT Stiffness - 0.80 - 0.70	Max. load 0.94 0.88	Work in traction 0.88 0.79	Wet-HT <sup>a</sup> Stiffness 0.63 0.67	Max. load 0.98 0.97	Work in traction 0.94 0.93	
Variable HEM GLM XYL	Dry-HT Stiffness - 0.80 - 0.70 - 0.71	Max. load 0.94 0.88 0.89	Work in traction 0.88 0.79 0.80	Wet-HT <sup>a</sup> Stiffness 0.63 0.67 0.67	Max. load 0.98 0.97 0.97	Work in traction 0.94 0.93 0.92	
Variable HEM GLM XYL CELL	Dry-HT Stiffness - 0.80 - 0.70 - 0.71 0.92	Max. load 0.94 0.88 0.89 - 0.98	Work in traction 0.88 0.79 0.80 - 0.97	Wet-HT <sup>a</sup> Stiffness 0.63 0.67 0.67 - 0.51	Max. load 0.98 0.97 0.97 - 0.99	Work in traction 0.94 0.93 0.92 - 0.98	

Table 4Pearson correlationcoefficients for tensileproperties and chemicalcomposition based on tensiletests of micro-veneers inwater-saturated state

<sup>a</sup>Based on measurements in water-saturated state after intermediate oven-drying (rewet)

determined as the initial slope of the load-deformation curves, was not affected much by HT (Fig. 4a). Dry-HT resulted in a small increase in stiffness to a maximum of ca. 118% of the reference value, while the stiffness of wet heat-treated wood remained in the range between 87 and 110%. In contrast to the stiffness, HT affected the maximum load (Fig. 4b) and the work in traction (Fig. 4c) in conditioned state to considerable extent. Wet-HT resulted in a linear decrease of the residual maximum load and the residual work in traction as a function of the hemicelluloses content. When the hemicelluloses content was reduced to ca. 52% of the reference, a residual maximum load and a residual work in traction of ca. 39 and 17% were measured for wet heat-treated wood, respectively. Similar losses in maximum load and work in traction were also determined for dry heat-treated wood, but at a much higher residual hemicellulose content of ca. 84%. A further loss in hemicelluloses did not lead to a further loss in tensile properties. The rates at which the residual maximum load and the residual work in traction decreased as functions of the residual hemicellulose content were approximately the same for wet and dry heat-treated wood. Instead, maximum load and work in traction of dry heat-treated were approximately decreased by a constant factor compared to wet heat-treated wood within the observed range of residual hemicelluloses. The additional decrease in tensile properties by DryHT was especially notable after a treatment duration of 1 h. Although 97% of the initial hemicelluloses content remained after this treatment, the residual maximum load and the residual work in traction decreased to less than 70 and 40%, respectively.

The differences in the micro-tensile behavior between the two HT techniques were also observed by SEM. The fractured tracheid surfaces showed morphological differences between wet and dry heattreated wood that were both treated for 7 h, although the residual maximum load and the residual work in traction were nearly identical (Figs. 3, 4). The fracture surfaces of wet heat-treated wood (Fig. 5c, d) resembled the fractured tracheid cells of the reference veneers (Fig. 5a, b). The fracture surfaces were not completely smooth and had a number distorted and broken cell wall pieces or fibrillar structures still attached to the cells. After Dry-HT, however, the fractured surfaces were smooth and appeared almost as cut with a blade perpendicular to the fiber direction in most regions of the micro-veneers with nearly no cell wall pieces or fibrillar structures attached to the cells (Fig. 5e, f).

The course of the residual tensile properties measured in water-saturated state in dependence on the residual hemicellulose content did not differ much from the results of the micro-tensile tests in conditioned state (Fig. 4). Furthermore, the residual tensile properties of wet heat-treated wood in water-



Figure 4 Micro-tensile properties of the veneers in dry state after conditioning at 23 °C and 50% RH ( $\mathbf{a}$ - $\mathbf{c}$ ) and in wet state after water-soaking ( $\mathbf{d}$ - $\mathbf{f}$ ) in dependence on the residual hemicelluloses content. The tensile properties and hemicelluloses content are shown as a percentage of the respective average value of the reference samples (= 100%). Error bars show the standard deviation.

saturated state after the process and in water-saturated state after intermediate oven-drying (rewet) were nearly identical. The main difference compared to the tests in conditioned state was the continuous increase in residual stiffness with decreasing hemicelluloses content for dry heat-treated wood. Furthermore, tensile testing in water-saturated state reduced the differences in residual maximum load and the residual work in traction as functions of the hemicelluloses content between Dry- and Wet-HT (Fig. 4e, f). This was caused by the dependence of the tensile behavior of dry heat-treated wood on the moisture state during the tensile tests, which resulted in an increase in the residual tensile properties when tested in water-saturated state compared to the tests in conditioned state (Fig. 3d-f).

SEM observations of fractured tracheid cells also revealed differences between wet and dry heat-treated wood when the micro-tensile tests were performed with water-saturated veneers (Fig. 6). For reference and wet heat-treated veneers, the fractured cell walls were uneven with a number of broken cell wall pieces still attached to them (Fig. 6a-d). Often, lamellar, open structures were seen in the secondary cell wall, which differed from the appearance after the tensile tests of conditioned veneers. In contrast, the fracture surfaces in dry heat-treated wood were nearly identical to those observed after testing the veneers in conditioned state (Fig. 6e, f). The majority of tracheids had cleanly split perpendicular to the fiber direction with barely any broken cell wall pieces attached to the fractured surfaces.

## Discussion

The chemical analyses confirmed earlier studies on the difference between HT of wood in dry and watersaturated state [6, 26, 30, 31]. The presence of water catalyzed the hydrolytic cleavage of covalent bonds during the hydrothermal treatments wood [32]. This resulted in the facile cleavage of acetyl groups and the efficient removal of hemicelluloses even at mild treatment temperatures (140 °C), which was shown by the FT-IR spectra and the chemical composition data. Dry-HT required higher temperatures and longer treatment durations to remove the same quantities of hemicelluloses. However, the absence of water and the application of elevated temperatures have been suggested to be more favorable for repolymerization reactions that lead to the formation of additional covalent bonds and cross-links in the cell wall matrix [6, 30]. Dehydration of sugars to furan-type derivatives and their reaction either with themselves or the lignin are possible reaction pathways that result in the formation of "pseudo-lignin" and a more cross-linked cell wall matrix [6, 33, 34]. These reaction pathways were less facile during Wet-HT, because the presence of water and the low treatment temperature did not favor the dehydration of sugars to furan-type derivatives [35, 36] and because sugars and their degradation products may have diffused into the process water [37]. The similar increase in lignin content, despite a less intense





removal of hemicelluloses, was an indication of the formation of pseudo-lignin during Dry-HT. Further evidence for more facile repolymerization reactions was provided by the FT-IR-spectra. While the bands at ca. 1730 and 1231 cm<sup>-1</sup> decreased during Wet-HT by the deacetylation and removal of xylan [32, 38], no such decrease was found for dry heat-treated wood. Instead, the shift toward lower wavenumbers indicated the formation of new carbonyl groups or ester bonds, as discussed previously [6].

Modifications of the cell wall matrix via the formation of cross-links or changes in the polymer conformation, particularly under dry heat conditions, affect the properties of heat-treated wood significantly [39–42]. This was also illustrated in the present study by the higher effectiveness in reducing the wood MC by Dry-HT, particularly at high RH, despite a higher amount of residual hemicelluloses compared to wet heat-treated wood. While the MC reduction of wet heat-treated wood can be assigned to the decrease in accessible OH group concentration following the preferential removal of hemicelluloses, the MC of dry heat-treated wood was further reduced by an additional mechanism [37]. Although there is uncertainty about the exact nature of this additional mechanism, previous studies suggested that the various modifications of the residual cell wall matrix play a major role. Some studies explained that cross-linking reactions during Dry-HT enhance the cell wall matrix stiffness and restrict the expansion of the polymers to accommodate water molecules [30, 31, 43]. Other studies speculated that changes in the conformation of the matrix polymers hinder the relaxation of the cell wall polymers toward their thermodynamically most favorable arrangement [31, 37, 44].





Similar to the reduction in wood MC, the present study also showed differences in the change in tensile properties by the two HT techniques. The reduction in maximum load and work in traction of wet heattreated wood was well in line with the concept that hemicellulose removal interferes with the load-sharing capabilities of the cell wall [24, 25]. Given the presumed role of hemicelluloses to provide the interfacial stress transfer between cellulose fibrils and the cell wall matrix, their removal may have promoted interface debonding and the pull-out of fibrils at low energy dissipation. Such failure mode coincides with the SEM images that showed a number of cell wall pieces or fibrillar structures attached to the fractured tracheid surfaces of wet heat-treated veneers. However, the fracture surfaces of tracheids in dry heat-treated wood appeared very differently and this was in line the additional loss in maximum

load and work in traction when compared with wet heat-treated wood at the same hemicelluloses content. This showed that the loss in hemicelluloses was not the only factor in changing the tensile behavior of dry heat-treated wood.

The catastrophic and brittle failure of the cell wall in dry heat-treated veneers, which was shown by SEM, indicated a rupture of the cellulose chains rather than a failure via interface debonding and pull-out of the fibrils. Dry-HT may have promoted the scission of the cellulose chains, which has been shown previously by the decrease in the degree of polymerization (DP) of cellulose despite an increase in cellulose content [45, 46]. A decrease in cellulose DP also occurs during hot water extraction [47, 48]. However, it may be speculated that the mild temperatures applied during Wet-HT (max. 140 °C) in the present study limited the depolymerization to the water-accessible regions of the cell wall, which prevented an excessive decrease in cellulose DP. A correlation between the cellulose DP and the tensile strength has already been shown for gamma-irradiated wood [49]. Furthermore, a recent study showed that the loss in maximum load by heating Japanese red pine (*Pinus densiflora*) in dry state at 150 and 180 °C was nearly identical for the wood bulk and the cellulose microfibrils in the S<sub>2</sub> cell wall layer [19].

Nonetheless, there was also an effect of the more cross-linked cell wall matrix on the tensile behavior of dry heat-treated wood. A better preservation of the tensile properties under water-saturated conditions followed from the sorption behavior and the high efficiency of the cell wall matrix modifications in reducing the moisture uptake at high RH levels. Furthermore, the enhanced cross-linking presumably reduced the compliance and the failure strain of the cell wall matrix under tensile loads. Although a larger proportion of the applied tensile loads was sustained by the cellulose fibrils, the cell wall matrix experienced a similar strain. Thus, cell wall matrix modifications in dry heat-treated wood may have promoted the failure of the cell matrix at low strain levels, which potentially resulted in the rapid formation of cracks that propagated though the cell wall. Although further studies are required to fully understand the underlying modes of action, the present results showed that the changes in tensile behavior under different HT conditions cannot be solely assigned to chemical composition changes.

## Conclusions

The preferential removal of hemicelluloses was measured for HTs of wood in dry and in wet state. HT in dry state also promoted repolymerization reactions that caused an enhanced formation of bonds and cross-links in the cell wall matrix. This further reduced the uptake of moisture and preserved the tensile properties under water-saturated conditions. However, dry heat-treated veneers showed an additional loss in maximum load and work in traction when compared to wet heat-treated veneers at similar losses in hemicelluloses. This was supported by SEM observations of fractured tracheids that showed brittle fractures after HT in dry state. This supported the assumption that the removal of hemicelluloses as coupling agents within the cell wall was not the only factor in changing the tensile behavior of dry heat-treated veneers. Consequently, chemical composition changes were found inadequate to fully explain changes in tensile behavior of wood that was heat-treated under various conditions.

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## **Author contributions**

MA conceived the research and designed the experiments. MA prepared the micro-veneers, performed the heat treatments together with SK, and took the DVS measurements. MA conducted the tensile tests and analyzed the tensile data. HS performed the FT-IR measurements, analyzed the chemical composition and prepared the SEM samples. DA conducted the SEM measurements. MA, MA and DA interpreted the results. LR supervised the work. MA wrote the manuscript. All authors read and approved of the final manuscript.

#### Compliance with ethical standards

**Conflict of interest** There are no conflicts of interest to declare.

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