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Macro- and micro-mechanical properties of red oak wood (*Quercus rubra* L.) treated with hemicellulases

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Abstract

Red oak wood (*Quercus rubra* L.) samples were submitted to an enzymatic treatment with a commercial mixture of hemicellulases aiming at the selective depolymerization and removal of the hemicelluloses. Mechanical properties of treated samples were characterized and compared with untreated samples at two hierarchical levels. At the macrolevel, tensile properties revealed to be less sensitive to degradation of the cell wall matrix compared to compression and hardness properties. Results obtained through indentation at the microlevel indicated that hardness and the so-called reduced modulus of treated wood were significantly lowered. Accordingly, hardness and reduced elastic modulus have proven to be most sensitive to modification of the cell wall matrix by reducing the content of hemicelluloses. It is proposed that transversal and shear stresses, which are mainly carried by the cell wall matrix, are additional parameters having strong effects on elastic modulus obtained by nanoindentation. Micromechanical modeling was employed to confirm the observed changes. There is consistency between the measured and the modeled properties, obtained at both the microlevel and the macrolevel of wood.

Keywords: continuum micromechanics model; enzyme; hemicellulose; mechanical properties; modification; nanoindentation; red oak; stiffness; strength.

Introduction

The mechanical properties of wood are outstanding in comparison to its low density. This can be explained by the sophisticated hierarchical structure of wood both on the macro- and microlevel. The supramolecular architecture of the cell wall with its special chemical composition also here plays an important role (Fengel and Wegener 1989; Fratzl and Weinkamer 2007; Salmén and Burgert 2008). The mechanical properties of the anisotropic material wood as related to its structure are well understood at the macroscale but only scarcely at the microscale (Gibson and Ashby 2001; Salmén and Burgert 2008). One way to study the mechanical function and interactions of individual cell wall polymers is the selective elimination of components of the cell wall matrix. Then, the effect of the modification of the cell wall integrity on the mechanical properties can be tested at different scales of resolution.

Since Wimmer et al. (1997) introduced nanoindentation to wood science for characterization of micro-mechanical wood properties, various efforts were made to interpret the data and to understand their significance (Gindl and Schoberl 2004). Originally, nanoindentation was developed to investigate hard and thin metal films (Oliver and Pharr 1992; Fischer-Cripps 2000). Later, nanoindentation was adapted to soft, homogeneous, and isotropic polymers, as reviewed by VanLandingham et al. (2001).

The so-called reduced modulus is commonly determined by means of nanoindentation together with the material hardness. Owing to the anisotropic nature of the wooden cell walls and the three-dimensional stress status under the indenter tip, the reduced modulus is not directly comparable to the elastic modulus generated by other experimental techniques (Page et al. 1977; Burgert et al. 2003; Orso et al. 2006) or model calculations (Bergander and Salmén 2002). Therefore, nanoindentation on wooden cell walls is useful when performed for comparative purposes. In an ideal case, if specimens are submitted to various treatments, the other properties obtained from the same tree, board or even from the same annual ring should be identical.

Gindl et al. (2004) and Gindl and Schoberl (2004) demonstrated that the microfibril angle (MFA) can also have a pronounced effect on the reduced modulus. In contrast, cell wall hardness seems to be insensitive to MFA, which led to the conclusion that hardness is more a function of matrix properties governed by hemicelluloses and lignin or alternatively hardness of cellulose varies only little with regard to its orientation. We have shown a high dependency on sample orientation relative to the direction of indentation, which is influenced by the orientation of microfibrils relative to the indenter tip (Konnerth et al. 2009).

Macro-mechanical tests are usually performed to determine the properties in a single anatomical direction by applying a one-dimensional stress situation, e.g., a uniaxial tension test. Under the commonly used Berkovich indenter with a total included angle of 142.3°, a three-dimensional stress state occurs. Hence, the measured reduced modulus depends on properties that are different in all three anatomical directions (Jäger et al. 2009a,b). This means that the material behavior in longitudinal direction, which is dominated by the stiff cellulose chains, and in transverse direction (Swadener et al. 2001) both affect the reduced modulus. The cell wall properties in transverse direction, however, are dominated by the less stiff hemicelluloses (Bergander and Salmén 2002). The reduced modulus is therefore seen as a compound factor, which varies with the anatomical directions as well as the pertinent cell wall constituents.

Hemicelluloses are branched polysaccharides with a linear chain backbone and a lower degree of polymerization than cellulose. These polyoses are linked via hydrogen bonds to the paracrystalline cellulose regions, and covalently to lignin (Whistler and Chen 1991). At the molecular level, cellulose microfibrils are thought to be encrusted by lignin and hemicelluloses. The role of hemicelluloses contributing to strength is still vague. It has been shown by Winandy and Lebow (2001) and Curling et al. (2002) that in particular the degradation of shorter branched monomers along the main chains of hemicelluloses seem to be responsible for strength losses in wood exposed to hydrolytic chemical agents or early microbial decay stages.

Effects of enzymes such as hemicellulases, cellulases, or lignin peroxidases applied to solid wood are disputed with regard to size and penetrability (Srebotnik and Messner 1988; Blanchette et al. 1989a,b). In various studies done on different tissues several effects were detected (Maurer and Fengel 1992; Bhat 2000; Unbehaun et al. 2000; Goswami et al. 2008; Maijala et al. 2008). Militz (1993a,b) found that spruce wood treated with a range of enzyme mixtures – including hemicellulases – have improved penetrability. Apart from the details described by Goswami et al. (2008), significant effects on the mechanical behavior of enzymatically treated wood are not well known.

In the present study, a hemicellulase treatment was applied with the aim of achieving selective degradation of the hemicelluloses in the cell walls. Subsequent mechanical studies at the macro- and microscale should identify influences of the altered polymer networks on the bulk mechanical behavior of wood. In particular, the micro-mechanical cell wall properties expressed as the reduced modulus should be investigated.

Finally, a continuum micro-mechanics model developed by Hofstetter et al. (2005, 2006, 2007) should be adopted in combination with a model for computation of the reduced modulus (Jäger et al. 2009a,b) to predict the mechanical properties of the enzymatically treated wood. The following hypotheses should be examined: (1) selective removal of hemicelluloses from cell walls alter mechanical properties that are matrix dependent, (2) mechanical measurements performed at different levels of resolution deliver consistent trends, and (3) micro-mechanical modeling corresponds with experimental data.

Material and methods

Red oak wood (*Quercus rubra* L.) with a density of 684±44 kg m^{-3}, featuring a moisture content of 7.9±0.3%, was taken for preparation of the specimens. The accessibility of red oak for enzyme solutions is good because of its high permeability (lacking tyloses in the vessels) (Chen et al. 1998; Lu and Avramidis 1999).

Enzymatic modification

Enzymatic treatment was performed in an incubator for 10 days at 40°C. The specimens were infiltrated with the enzyme solution under vacuum for 1 h. Enzyme solution: a commercial mixture of different hemicellulases from Aspergillus niger (Sigma-Aldrich, USA); 200 U/g wood was dissolved in acetate buffer (100 mM) at pH 5. The treatment was interrupted by immersing the specimens in boiling water for 5 min. Then, specimens were gently dried in a climate chamber until equilibrium moisture content was reached. The intention was that long treatment time in combination with the subsequent short boiling would lead to an essential degradation of hemicelluloses and their removal from the matrix to a large extent with only minor alteration of the structures and contents of lignin and cellulose.

Specimen preparation

Specimens with dimensions of 14×7×7 mm^3 were prepared from the enzymatically treated and the control specimens for determination of Brinell hardness (HB) and for compression tests. For the tensile tests, at least 12 longitudinally oriented specimens were prepared for each group. Specimens for nanoindentation (NI) measurements were prepared according to procedures described by Konnerth et al. (2008). Dimensions: 2 mm in length, 2 mm in width, and 0.5 mm in thickness. Specimens were embedded in Agar low viscosity epoxy resin kit (AGAR Scientific Ltd., Stansted, UK) and a smooth surface was cut on a Leica Ultracut-R microtome equipped with a Diatome Histo diamond knife. The embedded and sectioned specimens were glued to metal discs prior to clamping it magnetically to the indenter stage.

Macro-mechanical tests

Brinell hardness (HB) HB was determined according to European standard DIN EN 1534 (2000), with a steel ball of 5 mm in diameter and a peak force of 120±1 N. Equipment: Zwick/Roell Z020 universal testing machine equipped with a 5 kN load cell. In total, 12 specimens of each type (treated and untreated) were examined perpendicular to grain.

Tensile tests Equipment: Zwick/Roell Z100 universal testing machine equipped with a mechanical extensometer (Macrosense, Zwick/Roell, Ulm, Germany) and a 100 kN load cell. Bone shaped tensile test specimens with a total length of 180 mm, a thickness of 3 mm, and a width of 8 mm in the reduced section were loaded at a cross head speed of 2 mm min^{-1}. Calculation of tensile strength: maximum load divided by the cross-sectional area. The elastic modulus was calculated by fitting a line to the data points recorded between 10% and 40% of the maximum force.

Compression tests Equipment: Zwick/Roell Z020 universal testing machine equipped with a 20 kN load cell. The samples were tested in longitudinal direction at a cross head speed of 1.5 mm min^{-1}. Compression modulus was calculated with the deformation recorded by the cross head disregarding machine compliance. The displacement was sufficiently accurate for comparative purposes, although the absolute data are underestimated with this type of measurement.

Micro-mechanical tests by nanoindentation (NI) Equipment: Hysitron TriboIndenter system (Hysitron Inc., Eden Prairie, MN, USA) equipped with a three-sided pyramid diamond indenter tip (Berkovich type). The system is capable of performing in situ scanning probe microscopy by using the indenter tip as the probe (Figure 1). Out of this mode, the desired indent position can be marked and executed, which is useful if accurate positioning is required.

On two specimens from each type (treated and untreated) between 6 and 10 indents were done. These indents per specimen were placed at two different positions. Experiments were performed in the load-controlled mode using a three segment load ramp: load application ended within 3 s, holding time was 20 s, and the unload time was 3 s. As recommended by Gindl and Schoberl (2004), the peak load was set to 150 μN for all indents, resulting in an indent size less than 1/3 of the cell wall widths (Figure 1). Through this measurement, the possible influence of the surrounding embedding material on the obtained data was kept to a minimum. Load-indentation depth curves recorded during the NI experiments were evaluated according to Oliver and Pharr (1992) as described by Konnerth and Gindl (2006). This method yields the reduced modulus of elasticity derived from the initial slope of the unloading curve and the cell wall hardness.

Model prediction

A continuum micro-mechanics model was employed (Hofstetter et al. 2005, 2006, 2007). Effects from moisture content (MC) on mechanical properties were implemented by introducing poromechanics framework (Bader et al. 2010). The applied model provided estimates for the elastic stiffness tensor at four different scales of resolution: (1) at the smallest scale, the effective properties of the matrix network (i.e., hemicelluloses, lignin, water, and extractives) as well as the cellulose microfibrils, which consists of a crystalline core with a paracrystalline shell, were modeled. (2) The cell wall material was modeled as a composite of cellulose microfibrils embedded in a poroelastic matrix network. The microfibril angle (MFA, i.e., the inclination of the MF relative to the longitudinal cell wall axis) was also considered. (3) Softwood material is modeled by a honeycomb structure consisting of cell wall material. This takes account for the fact that the mechanical behavior of wood is different in longitudinal, radial, and tangential directions. (4) Hardwood specific anatomy was also considered as vessels and ray cells were embedded in the contiguous matrix built up by parenchyma cells and tracheids (Bader et al. 2010). These small cell types are summarized and considered in the model as softwood type porous material. Vessels are modeled as pores with circular cross-sections oriented in the longitudinal direction. A mean diameter and an equal distribution of vessels are assumed. Ray cells are oriented in the radial direction and are implemented in the model as equally distributed cylindrical inclusions with elliptic cross-section (aspect ratio 1:5) consisting of soft wood type material.

The micro-mechanical model allowed the consideration of chemical and structural variability of various wood species. Also, degradation of selected components by, e.g., fungal decay or enzymes can be implemented in the model. The longitudinal modulus of the enzymatically treated red oak and the control, respectively, will be predicted with this model. To estimate the reduced modulus obtained from nanoindentation, the model suggested by Jäger et al. (2009a,b) was employed. During indentation, a three-dimensional stress status evolves within the sample with shear stresses as well as transverse stresses present in the sample. Both the stress status and the transverse isotropic behavior of the S2 layer are considered. The latter was deduced from the parallel arrangement of the cellulose microfibrils. With the stiffness tensor for cell wall material, which was modeled by the aforementioned micro-mechanical model, the reduced modulus was estimated.

Model input parameters

Composition of red oak and MFA data were taken from the literature (Wagenführ 2007) (Table 1). To compute the chemical composition of the NI tested S2 layers, the distribution of chemical components within the cell wall was employed as reported by Fengel (1969, 1970) (Table 1, S2 layer). MFA was set to a mean of 10°. Spiral grain angle describing the deviation of the oriented fibers from the

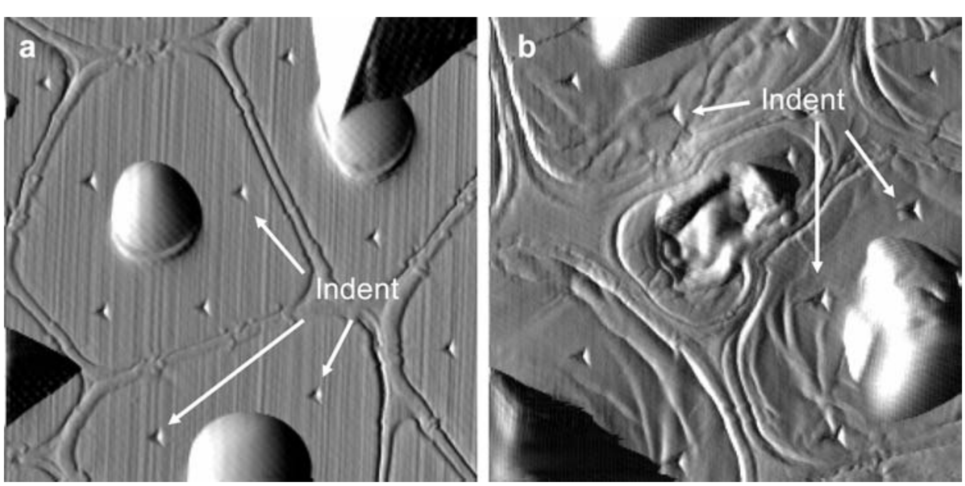

Figure 1 Scanning probe microscopy (SPM) images of reference (left) and enzymatically treated (right) wood cell walls (image size 20×20 μm). The cell wall surface topography is flat (a) and rough (b). The indents from nanoindentation experiments are clearly visible in S2.

main stem direction of the tree is considered in the micro-mechanical model as well. Grain angles were determined for tensile specimens and varied between 0° as the minimum, to 3.7° as the mean, up to 9° as the maximum value.

Density (684 kg m^{-3}), MC (7.9%), proportions of vessels (13%), and ray cell proportion (10.3%) were kept constant in the modeling approaches. For the mechanical properties of the constituents of the untreated samples, the data published by Hofstetter et al. (2005) were used. The elastic modulus for the hemicelluloses was set to zero in the enzymatically treated samples as no information about the degree of depolymerization was available. This simplification gives a lower limit for the estimated stiffness of the treated samples.

Results and discussion

Enzymatic treatment considerably influenced the mechanical properties of red oak depending on load direction and the applied testing method. The longitudinal modulus in tension (Figure 2) showed only slightly decreased values for the enzymatically treated specimens with differences being not significant (t-test, $P > 0.05$). Tensile strength (Figure 2) of the treated specimens showed slightly higher values than the control, although the results are not significant ($P < 0.05$). In contrast, compression tests for the treated samples were significantly reduced for both elastic modulus and strength. It should be noted that the absolute values of compression modulus are underestimated as the deformation was recorded by the cross head only and the machine compliance was not taken into account. Overall, strength and stiffness degradation of the treated specimens were only visible in compression mode, while lacking in tension.

Mechanical losses in the case of diminished content of hemicelluloses in the cell wall was hypothesized and confirmed in the compression mode. In tensile mode, the widely unaffected cellulose with its long chains is known to dominate the properties in longitudinal direction (Bergander and Salmén 2002). Under compression, the matrix material in the cell walls has a stabilizing (crosslinking) effect on the cellulose micro- and macrofibrils, thus it is consequent that hemicellulose losses deteriorate the performance under such conditions. Within a weakened matrix the cellulose chains can bend or even buckle and this leads to a significant decline of both stiffness and strength. Tensile strength tended towards higher values in the treated samples, but these values are seen as less reliable as they are more prone to notches and defects. This also explains the wider scattering of the tensile data.

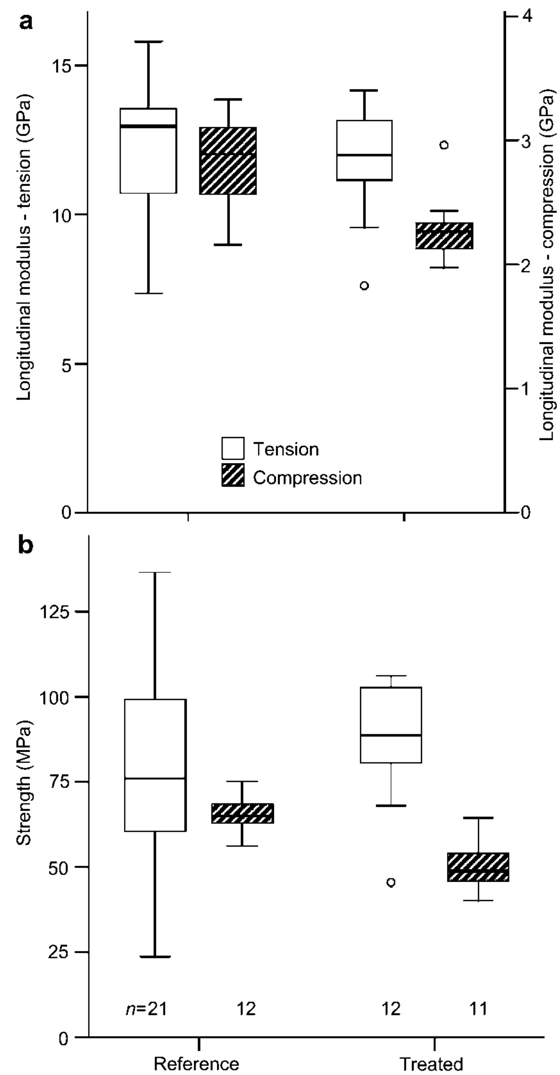

Figure 2 Longitudinal modulus (a) and strength (b) in tension as well as in compression of untreated reference and enzymatically treated red oak wood. n = Number of specimens tested.

Table 1 Input parameters for macro- and micro-model: chemical composition, microfibril angle (MFA) and grain angle (compiled from Wagenführ 2007).

		Cellulose[a] (%)	Hemi-celluloses (%)	Lignin (%)	Extractives (%)	MFA (°)	Grain angle (°)
Macro-model (cell wall)	Min	40.5	27.7	26.5	5.3	15	9
	Mean	45.0	27.7	22.0	5.3	10	3.7
	Max	49.5	27.7	17.5	5.3	5	0
Micro-model (S2 layer)	Min	49.2	21.7	23.2	5.9	20	–
	Mean	53.8	21.4	19.0	5.8	10	–
	Max	58.3	21.0	14.9	5.7	0	–

[a]Paracrystalline and crystalline.

To assure the actual positioning of the indents, scanning probe microscope images (Figure 1) were made from the ultra-microtomed cross-sectional surfaces. These images already revealed clear differences in surface topology between the untreated and the treated wood cells: surfaces of the latter were less smooth than in the former. The inhomogeneous cutting properties of the partially degraded cells could explain this observation.

Data of reduced modulus and hardness obtained by NI are presented in Figure 3 (left and middle). The treated samples show decreased values for both parameters. Similarly, Brinell hardness tested on the macroscale also showed reduced values at the same order of magnitude. This supports hypothesis 2 postulating that the mechanical measurements performed at different levels of resolution should deliver consistent trends.

With the assumption that hemicelluloses were at least partly degraded, the found effects for hardness obtained by nanoindentation comply well with corresponding literature data. Hemicelluloses are described as acting widely as a matrix related component (Gindl et al. 2004). The reduced modulus from NI, which is known as sensitive to cellulose properties as well as MFA (Gindl and Schoberl 2004), did show reductions that amounted to 50% for the treated specimens. This reduction is remarkable and can be interpreted that not only properties in longitudinal direction plays a role in these experiments: transverse properties could also have contributed to the measured reduced modulus. Because a multi-dimensional stress status occurs during indentation, the enzymatically altered matrix has mostly affected the NI derived reduced modulus (Gindl and Schoberl 2004).

Experimental results were compared with the performed model calculations done at both the macroscale and the microscale level (Figure 4). Tensile modulus and reduced modulus are plotted and compared with the mean, minimum, and maximum values predicted by the model. A strong agreement between the data is evident. Tensile moduli of the untreated samples were slightly overestimated, whereas for the treated samples the modeling coincided excellently with the measured values. The predicted moduli differences between the treated and the untreated samples were comparable to those obtained experimentally (20% vs. 10%, respec-

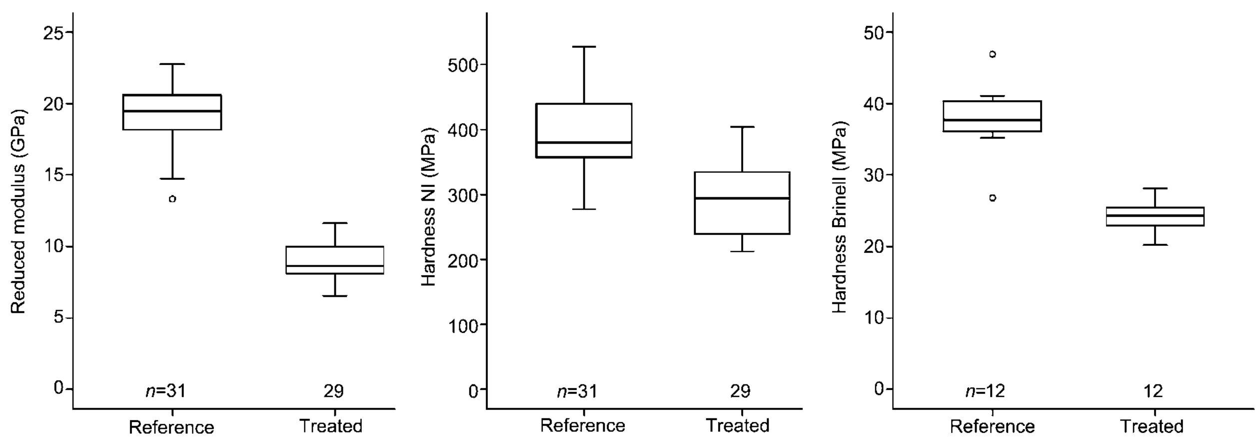

Figure 3 Reduced modulus (left) and hardness (middle) measured by nanoindentation. Brinell hardness (right) of enzymatically treated red oak wood vs. untreated control. n = Number of indents performed and specimens tested in the case of Brinell hardness.

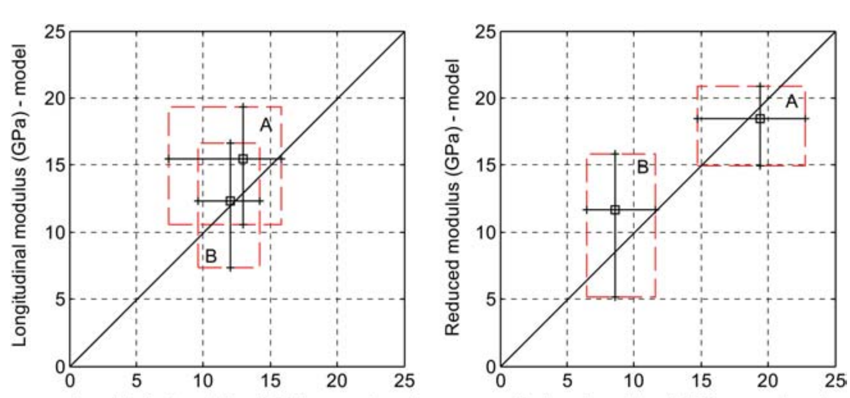

Figure 4 Comparison between modeled and experimental results (indicating quality of model prediction) of longitudinal modulus (left) and reduced modulus (right). (A) Untreated control and (B) enzymatically treated red oak wood. In the case of model results small boxes represent mean, whiskers minimum and maximum values. For experimental results, the small box denotes 50% percentile (median), whiskers represent 25% and 75% percentile.

tively). From this result it can be concluded that the longitudinal load bearing in tension was carried mainly by the stiff cellulose with little dependency of the matrix including hemicelluloses. As regards compression tests, a comparison between model prediction and experiment has not been performed. The employed model is not able to account for effects such as local buckling of cell walls which might occur during compression loading and which influences the compression modulus.

At the cell wall level of the untreated samples (Figure 4, right), the model predictions also showed good agreement with the experimental data. The reduced modulus of the enzymatically treated sample was slightly overestimated. However, the shown large difference in reduced modulus between treated and untreated sample was predicted well by the model. In summary, the findings confirm hypothesis 3, predicting that micro-mechanical modeling is in correspondence with the experimental data even at different structural hierarchies (Fratzl and Weinkamer 2007).

Findings related to nanoindentation technology

As mentioned, the lowering in the reduced modulus obtained by NI was more pronounced than the reduction in longitudinal modulus. This can be explained by the three-dimensional stress nature that occurs during indentation, and which creates significant transverse and shear stresses. The resulting deformations strongly depend on these transverse and shear stress properties of the cell wall, as they are governed by the matrix consisting of hemicelluloses and lignin (Keckes et al. 2003; Fratzl and Weinkamer 2007). Hence, the lost matrix integrity of the treated specimens resulted in higher deformation and reduced cell wall stiffness. This means that the reduced modulus obtained by NI is significantly driven by the cell wall matrix. In summary, transverse and shear stresses, as they occur under the three-dimensional stress status in the vicinity of the indenter tip, have contributed to the reduced modulus to a much greater extent than expected.

Conclusion

In this study the mechanical properties of both the untreated control and the enzymatically treated red oak wood samples were characterized at two hierarchical levels. As a consequence of the selective removal of the matrix polymer hemicelluloses, a diminishing of mechanical wood properties was demonstrated for different loading modes. Tensile properties revealed to be less sensitive to matrix degradation compared to compression or hardness properties. Hardness and reduced modulus obtained through indentation were significantly lowered in the case of treated wood. Hardness has proved to be sensitive to changes in the cell wall matrix composition. Overall, reduced modulus has shown the strongest change with modification. It is therefore proposed that transversal and shear properties, which are mainly driven by the matrix, are additional parameters having strong effects on the reduced modulus. The observed tensile modulus as well as the reduced modulus obtained through nanoindentation was predicted by a micro-mechanical model. This approved the consistency of the measured properties obtained at the micro- and the macrolevel.

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