Delignified and Densified Wood - A Versatile Concept for New High-Performance Wood-Based Materials

Doctoral Thesis

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Delignified and Densified Wood – A Versatile Concept for New High-Performance Wood-Based Materials

A thesis submitted to attain the degree of
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(Dr. Sc. ETH Zurich)

presented by

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Summary

Nature designs ingeniously engineered biological materials from a rather limited amount of elements. Trees, for example, evolved a sophisticated wood structure, which has been optimized for vital functions such as water transport and mechanical support. As a result, wood is a lightweight, open porous material with high specific mechanical properties and is therefore an attractive material.

In recent years, research activities towards new material concepts based on wood have strongly increased due to competitive advantages of the hierarchical structure and the materials sustainability. Especially the interest in materials derived from structure-retaining delignification of wood gained substantial interest. Structure-retaining delignification removes matrix components but aims at keeping the cellulose arrangement and hierarchical architecture of native wood, which lends the material its high stiffness and strength. The obtained scaffolds possess an open-porous path consisting of lumina and pits and additionally, cell wall porosity in wet state is much higher compared to native cell walls. This eases functionalization and led to the development of new functional cellulose materials. Cellulose scaffolds are shapeable in wet state due to the removal of lignin and can be densified for increasing the fiber volume fraction and therefore mechanical properties. These characteristics paved the way for densified cellulose materials, including tunable fiber alignment along with mechanical and functional gradients, which are developed and discussed in-depth in this doctoral thesis.

The primary goal of this work was to directly make use of the wood inherent cellulose scaffold by structure-retaining delignification and to utilize the obtained scaffolds as structural material. First, a strategy for delignification and densification of wood was developed and the influence of parameters such as humidity of the cellulose scaffold and densification forces on mechanical performance were investigated. Strongly densified matrix-free cellulose scaffolds showed superior tensile properties compared to wood and many other natural fiber-reinforced composites mainly due to strong fiber-fiber interactions. We further investigated the moisture triggered formability of the scaffolds, which allowed fabrication of shaped structural components that are optimized towards external loading conditions. In wet state, water swells the cell walls and forms a water layer between neighboring cells that enabled shear deformation and adjusted fiber alignment to reduce stress concentrations. Structural rigidity was gained by drying in a reversible process. Mechanical gradients were incorporated into the material to further optimize for mechanical
performance. These gradients were achieved by adjusting the materials density and were manufactured by topographic stacking or local densification of delignified wood layers. A combination of functional and mechanical gradients was exemplarily shown by asymmetric, staircase-like stacking of magnetically functionalized delignified wood followed by densification.

Efficient and scalable shaping and densification of wet delignified wood was enabled by a newly developed vacuum shaping technique. In this process, wet delignified veneers are draped onto a porous mold in a defined lay-up and are densified by vacuum in a vacuum bag. The use of a water-based adhesive (starch) between delignified veneers allowed for manufacturing all-bio-based composite parts. The cellulose-starch composite is recyclable and disintegrates in water, which is beneficial regarding end-of-life use. However, the hydrophilicity of the composite leads to reduced mechanical performance when in contact with water, which makes coatings or polymer infiltration necessary. To account for this, interpenetrating wood-polymer composites were manufactured by infiltration of epoxy into delignified bulk wood followed by densification. The infiltration of the hydrophobic matrix into the hydrophilic cellulose scaffold were conducted in a vacuum assisted approach and isostatic densification of infiltrated scaffolds in closed molds further improved the mechanical performance of the composite part by increasing the fiber volume content up to 80%. Tensile stiffness values of high fiber volume content composites were found to exceed values calculated by the simple concept of the rule of mixtures. This suggests that more complex phenomena comprising enhanced mechanical interlocking between neighboring fibers with higher fiber volume content are contributing to the high stiffness of the composites.
Zusammenfassung


Zusammenfassung


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List of Abbreviations

1D, 2D, 3D, 4D  one-, two-, three-, four dimensional
AFM  atomic force microscopy
CA  contact angle
CFRP  carbon fiber reinforced polymer
CO₂  carbon dioxide
CRTM  compression resin transfer molding
DCM  densified cellulose material
DSC  dynamic scanning calorimetry
DVS  dynamic vapor sorption
DWRP/DWRC  delignified wood reinforced polymer/composite
Fe₂O₃  maghemite
Fe₃O₄  magnetite
FRP/FRC  fiber reinforced polymer/composite
FTIR  Fourier transform infrared spectroscopy
FVC  fiber volume content
GFRP/GFRC  glass fiber reinforced polymer/composite
HAc  acetic acid
HF  high force
H₂O₂  hydrogen peroxide
IPC  interpenetrating phase composite
LF  low force
LM  light microscopy
NFRP/NFRC  natural fiber reinforced polymer/composite
PA  polyamide
PDMS  polydimethylsiloxane
PFOTS  trichloro (1H, 1H, 2H, 2H-perfluorooctyl)silane
PLA  polylactic acid
PMMA  polymethylmetacrylate
PP  polypropylene
RH  relative humidity
ROM  rule of mixtures
RT  room temperature
SEM  scanning electron microscopy
TFH  tetrahydrofuran
TGA  thermogravimetric analysis
TiO₂  titanium dioxide
UD  unidirectional
VARI  vacuum assisted resin infusion
XRD  X-ray diffraction
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1 Motivation and Objectives

Wood is a hierarchical material, which is optimized to combine vital functions for the living tree including water and nutrient transport and mechanical support. It is a multiscale fiber reinforced composite consisting of elongated cells embedded in a matrix of lignin and pectin. On cell wall level, cellulose fibrils provide strength and the matrix, consisting of lignin and hemicelluloses, acts as the glue. The concept of embedding stiff reinforcing elements in a compliant matrix has been inspiration for the development of man-made fiber reinforced composites such as glass fiber- (GF), carbon fiber- (CF) or natural fiber reinforced composites (NFRCs). Continuous glass fiber reinforced composites (GFRCs) are for example used in aerospace, construction or automotive industries due to their good mechanical properties and low weight. However, these composites are energy intense in the production and difficult to recycle. Hence, it necessitates sustainable alternatives. In this regard, natural fibers are increasingly considered as an alternative due to their comparable strength combined with recyclability and low energy consumption in production.

Typical strategies to gain high in-plane performance of fiber reinforced composites comprise increasing the fiber volume content or optimizing the stress-transfer between fiber and matrix. Both strategies, however, face certain limitations. The maximum fiber content is theoretically 70% and usually this cannot be surpassed because of the need of polymer-matrix between neighboring fibers for stress transfer. Practically, the maximum fiber content is around 63-65% for GFRCs and usually even lower for NFRCs due to reduced packing density as a result of inhomogeneities in fiber orientation, shape and/or diameter. The stress-transfer at the fiber-matrix interface is crucial for a high-performance of the composite part and can be enhanced by chemical modifications and by mechanical roughening of the fiber surface.

However, natural materials such as wood still outperform man-made composites in terms of complex microstructural design and resulting property combinations. Especially the development of hierarchical structures, which is a common design principle in natural materials, is still very challenging for man-made composites. One way to circumvent this problem is to use biological materials such as wood in top-down approaches and to profit directly from natures design. This direct use of wood after modification comes with the advantage that the hierarchical structure is already provided. A top-down approach that has gained increasing attention is structure-retaining delignification of wood, which results in a lightweight, porous cellulose scaffold that consists of
unidirectionally-aligned cellulose fibers. In dry condition, the scaffold is mechanically robust due to strong fiber-fiber interfaces and comprises an open porous path, which can be used for functionalization or matrix infiltration. Delignified wood has been used as reinforcing component in high-strength wood-based materials\textsuperscript{2,10} but also in new functional materials such as filters\textsuperscript{11} or transparent materials.\textsuperscript{12,13}

The use of cellulose scaffolds as load-bearing component is investigated in detail in this thesis. Strong fiber-fiber interfaces in the scaffolds are responsible for stress-transfer between neighboring fibers and make the polymer-matrix, which traditionally is responsible for stress-transfer, unnecessary at this location. In combination with the deformability of delignified wood cells, this stress-transfer at the fiber-fiber interface leads to the possibility of exceeding the maximum theoretical fiber volume content and thus has the potential to pave the way towards novel natural fiber reinforced materials, which could outperform traditional composite concepts.

The main research objectives of this thesis are summarized as follows:

- Detailed investigation of cellulose scaffolds produced by structure-retaining delignification of wood. This includes a detailed study on the influence of humidity on microstructure and mechanical properties and concepts for tuning mechanical and functional properties.

- Investigation and utilization of the interconnected porous network of the cellulose scaffold as a path for polymer matrix infiltration and in-depth characterization of the microstructure and mechanical properties of the resulting delignified wood reinforced polymers compared to traditional fiber reinforced composites.

- Development of scalable and versatile methods to fabricate delignified wood-based materials inspired by already existing composite processing techniques and gathering of the limits of these techniques.
2 Outline of the Thesis

This cumulative thesis mainly consists of four articles exploring the concept of structure-retaining delignification of wood followed by densification for the development of wood-based high-performance materials. A short introduction into fiber reinforced composites and wood is given in chapter 3.1. and 3.2, respectively. Then, delignification of wood and material concepts based on structure-retaining delignification reported in literature are introduced for background information in chapter 3.3. The articles published in the framework of the thesis are presented in chapter 4.

The first article “Delignified and Densified Cellulose Bulk Materials with Excellent Tensile Properties for Sustainable Engineering”\(^\text{14}\) presents the general concept of delignification followed by densification (chapter 4.1). A detailed investigation of mechanical properties of densified cellulose scaffolds is conducted and cell wall folding patterns are analyzed at tissue and cell wall level by using light-microscopy and AFM. The effect of a newly developed shear-assisted densification on the materials morphology is analyzed. Additionally, the ability to shape the material in wet state is described in this article.

The second article in chapter 4.2 is about “Tunable Wood by Reversible Interlocking and Bioinspired Mechanical Gradients”\(^\text{15}\). In this article, wood is turned into a versatile engineering material by delignification, wet shaping and spatially tuning of the mechanical and chemical properties. Biological design principles such as density gradients and fiber alignment are implemented to optimize for external loading conditions. Moisture-

\[\text{Figure 2-1: Illustration of the Densified Cellulose Material (DCM) manufactured in a two-step process combining delignification and densification.}\]\(^\text{14}\)

\[\text{Figure 2-2: Illustration of the transfer of nature’s design principles such as fiber alignment and density gradients into delignified wood.}\]\(^\text{15}\)
triggered reversible interlocking between wood cells provides formability in wet state and high strength and stiffness in dry state.

Chapter 4.3 describes the “Fabrication and Design of Wood-Based High-Performance Composites”\(^\text{16}\). In this video publication, we present two versatile fabrication routes to manufacture shaped Densified Cellulose Material (DCM) parts, namely simple densification in closed molds and vacuum processing in open molds. The newly developed open-mold vacuum processing allows for a scalable production of DCMs targeting for example the automotive industry or aviation. In addition to the article, a patent application (Patent No. 19187447.8 - 1018) was filed.

The fourth article in chapter 4.4 “Delignified Wood-Polymer Interpenetrating Composites Exceeding the Rule of Mixtures”\(^\text{17}\) describes the manufacturing of Delignified Wood Reinforced Polymers (DWRPs) by polymer infiltration into a delignified wood scaffold followed by densification. The infiltration process is studied in detail and tensile and bending properties of DWRPs are compared to reference systems such as glass fiber reinforced composites and matrix-free DCMs.

Additionally, a summary of the co-authored publication “Mesoporosity of Delignified Wood Investigated by Water Vapor Sorption” is given in chapter 4.5. This article provides a detailed characterization of cell-wall porosity in partially and completely delignified wood at different moisture contents, which adds valuable information for further functionalization of the material.

A general discussion and conclusion of the articles is presented in chapter 5 and the outlook in chapter 6 demonstrates future research potential in the field of wood-based composites.
3 Introduction

3.1 Fiber reinforced composites

Composite materials are increasingly considered in many structural components due to their high specific mechanical properties. Especially for weight-critical parts with dimensional restrictions in the automotive industry or in aviation, composite materials possess compelling advantages and are progressively replacing metals.\textsuperscript{18}

A composite material is defined as a combination of two or more materials on a macroscopic scale. By appropriate design, the properties of the composite far exceed those of the single components.\textsuperscript{19} Fiber reinforced composites follow the concept of embedding stiff reinforcing elements in a continuous matrix, a design principle that is also often observed in natural materials such as wood or bone.\textsuperscript{20,21} These natural hierarchical materials exhibit high stiffness, strength and toughness at low weight, resulting in very high specific mechanical properties and act as role models for synthetic fiber reinforced composites.

3.1.1 Microstructure and composition

For manufacturing synthetic fiber reinforced composites, continuous fibers are typically embedded in a polymer matrix in a unidirectional alignment. Figure 3.1.1 illustrates a typical architecture of a unidirectional fiber reinforced composite. The composite part can be tailored regarding the final loading condition by adjusting fiber orientation, choosing fiber and matrix type and by modifying the interface.

Choice of fibers

Load-bearing fibers range from synthetic (e.g. glass fibers, carbon fibers) to natural (e.g. hemp, flax, wood) and differ in mechanical performance and in price.\textsuperscript{22} Glass fibers are utilized for example in sports equipment, boat shells or in aviation as they provide high strength and stiffness and corrosion resistance at low cost. Since the 1990s, however, plant-based fibers such as hemp or flax but also wood-based fibers are increasingly considered as sustainable alternative to glass
fibers. Further advantages of natural fibers include their low density resulting in high specific strength, low abrasiveness, biodegradability and lower cost compared to glass fibers. However, limitations such as high moisture absorption, the variability in mechanical properties resulting from seasonal variations and the poor adhesion to thermoplastic matrix systems still have to be improved.

Choice of matrix
Fibers are surrounded by a duroplastic or a thermoplastic matrix, whose functions include to provide structural support to the fibers, to protect them from abrasion on neighboring fibers and to transfer stress throughout the composite part. Duroplastic resin systems such as epoxy are irreversibly hardened after curing via chemical cross-linking, which results in a stiff material and good stress-transfer within the composite material. However, duroplastic systems are brittle and do not resist crack propagation. Alternatively, thermoplastic matrices (e.g. polypropylene (PP), polyamide (PA)) offer higher toughness. Additionally, they can be remolten, enabling re-shaping and eased recycling of the composite part. But high melt viscosity of thermoplastics or high processing temperatures limit processability. The fiber-matrix bonding with thermoplastic polymers is based mainly on physical and mechanical interactions, which result in weaker interfaces and reduced stress-transfer compared to duroplastic matrices that are based on chemical bonding.

Interface modification
The fiber-matrix interface is important for stress transfer throughout the composite part and is often modified in order to optimize bonding. Glass fibers for example are modified by coatings that contain lubricants for eased handling and coupling agents for enhanced chemical bonding between fiber and matrix. Also natural fiber pre-treatments are indispensable due to the hydrophilic nature of the fibers and the typically hydrophobic character of matrices which results in low interfacial interactions. If thermoplastic matrices are used, wetting of the fiber is more critical due to the higher viscosity compared to duroplastic systems and modification of the interface is even more important. Surface modification of natural fibers include dewaxing, alkali treatment, peroxide treatments and the addition of coupling agents such as maleic anhydride. Coupling agents bind covalently to the fiber and change the surface energy to increase physical interactions with the matrix. Additionally, long polymer chains attached to the fiber surface, for example by maleic anhydride coupling, can increase the bonding at the interface. Other strategies
include improving fiber separation after harvesting in order to enhance the interfacial fiber-matrix area in the composite\textsuperscript{31} and fiber roughening, which enlarges fiber surface area and at the same time facilitates mechanical interactions. Roughening is either achieved by the addition of particles or smaller fibers or by hierarchical structuring.\textsuperscript{7,8,32}

3.1.2. Mechanical properties

Apart from the choice of fiber, matrix and interface design, one of the main factors determining mechanical performance is the fiber volume content (FVC). It directly influences stiffness, strength, thermal expansion or moisture adsorption.\textsuperscript{18,33} The enhancement of properties such as stiffness with higher FVCs can be expressed by simple models, which help in estimating the final performance of a composite.

Rule of mixtures

The rule of mixtures (ROMs) is the simplest model to estimate Young’s modulus or other properties such as mass density of a continuous, unidirectional composite. For the ROM of elastic properties, an equal strain assumption (Voigt model) and an equal stress assumption (Reuss model) have been employed.\textsuperscript{34-36} The equal strain assumption works well for aligned continuous fiber composites in fiber direction, for which the basic assumption of equal strain in matrix and fibers is correct and defines the so-called upper bound of the ROMs. The Reuss model defines the lower bound and describes the behavior of a unidirectional composite perpendicular to the fiber direction (\(E_2\)), where matrix and fiber experience the same stress. Figure 3.1.2. graphically shows the upper and lower bounds. Assuming well-bonded reinforcements, all composites show a Young’s modulus between the lower and upper bound ROMs.\textsuperscript{25}
Introduction

\[ E_1 = E_f V_f + E_m V_m \]  \hspace{1cm} (1)
\[ E_2 = \frac{E_f E_m}{E_f V_m + E_m V_f} \]  \hspace{1cm} (2)

Where \( E_1 \) and \( E_2 \) are the upper and lower moduli of elasticity of the composite, respectively, \( E_f \) represents the modulus of elasticity of the fiber, \( E_m \) is the modulus of the matrix and \( f \) represents the volume fraction of the fibers.

**Halpin-Tsai equation**

Halpin and Tsai developed a semi-empirical model for predicting the elastic properties, which additionally takes the geometry and packing arrangement of the reinforcing fiber into consideration.\(^{25}\)

\[ E_c = E_m \left( \frac{1 + \zeta \eta f}{1 - \eta f} \right) \]  \hspace{1cm} (3)
\[ \eta = \frac{E_f - 1}{E_m \zeta} \]  \hspace{1cm} (4)

Where \( E_c \) is the modulus of elasticity of the composite and \( \zeta \) is a parameter that depends on the geometry of the filler with regard to the loading direction as follows:

- \( \zeta = 2 l / d \) for the longitudinal modulus
- \( \zeta = 2 \) for the transverse modulus

Where \( l / d \) is the aspect ratio of the filler.

Therefore, if the length of the filler approaches zero, the Halpin-Tsai equation reduces to the lower bound ROM. In contrast when the length of the reinforcing fiber approaches infinite length, the equation reduces to the upper bound model.

Following theoretical models such as the ROMs or Halpin-Tsai, the FVC should be increased up to 100% to optimize strength and stiffness. However, in traditional composite manufacturing, this content can neither theoretically nor practically be obtained and is limited to approximately 63-65%.\(^3\) Other strategies to optimize mechanical performance include the adaptation of fiber alignment and tailored interface design and will be discussed in the next chapter.
3.1.3. Tailoring mechanical properties by bioinspired design

Nature has evolved structural composites with heterogeneous architectures including complex design principles to locally tune mechanical or functional properties. Design principles have been summarized by Naleway et al. 2015 into eight main categories, namely fibrous-, helical-, gradient, layered-, tubular-, cellular-, suture- and overlapping structures. In this chapter, we focus on laminates comprising helical design aspects and suture structures, as these concepts can be easily incorporated into delignified wood based materials.

Laminates

So-called twisted-ply structures are observed in biological role models, for example in the exoskeleton of grasshoppers or in fish scales. The incorporation of such bioinspired helical structuring into composite materials is achieved by laminating techniques. By aligning reinforcements at varying angles, in-plane isotropy and increased toughness are obtained. The principle material direction of each layer needs to be adjusted according to the final parts needs, enabling to tailor the directional dependence of strength and stiffness of a man-made composite material. Plywood is a typical wood-based composite material where this laminate manufacturing is applied. Thin layers of wood veneers are glued with alternating 0°/90° ply orientation, resulting in isotropic properties in the two main axes. Other products additionally have plies in steps of 45° to render the material more isotropic.

Figure 3.1.3. illustrates layers that are oriented in 0°, 45° and 90°. Common lay-up techniques in composite design comprise unidirectional (0°), cross ply (0°/90°), or quasi-isotropic (0°/±45°/90°) laminates. Laminate manufacturing is exemplarily shown in the third article (chapter 4.3) for starch-cellulose composites.

Sutures and interlocking

In biological materials, a sophisticated interplay of hierarchical structures and interfaces often results in remarkable performance and property combinations such as toughness, strength and stiffness, which are difficult to achieve in engineering materials. Tailored interfaces improve fracture resistance of brittle materials by deflecting or channeling cracks, for example through a protein layer in nacre, or they increase deformability by tailoring the shape of the weak interface.
These weak interfaces often exhibit characteristic wavy and interlocked patterns, so-called suture structures. Suture interfaces are able to combine high strength with low strain formability as observed for turtle shells. In the carapace of the red-slider turtle, adjacent ribs of the turtle shell are connected by a suture interface. A thin soft-tissue interface remains between the ribs, which equips the shell with flexibility at low-rate deformations, but make it rigid at high-rate loads and large deformations. Other suture interfaces allow for local energy dissipation as for example observed in the woodpeckers’ beaks.

Suture lines vary in geometry and can create interlocked architectures, as found in the tissue of walnut shells. Antreich et al. 2019 reported that each polylobate sclereid cell, an irregularly lobed cell with concave and convex parts in the walnut shell, is interlocked with neighboring cells. This interlocking results in a “3D puzzle” with high ultimate tensile strength.

Interfacial design in synthetic fiber reinforced composites is of high importance, determining the composite part failure mechanism, and needs to be correctly adjusted depending on the final application. Suture or interlocking models as observed in natural materials can act as role models and may influence the way we design composite materials in the future. Malik et al. recently reported bio-inspired “jigsaw”-like interlocking sutures, which enhance mechanical properties of inherently brittle materials such as ceramics and Libanori et al. produced tough, nacre-like bulk ceramics by using mechanical interlocking of surface-roughened microplatelets as an efficient energy dissipation mechanism. Interlocked interfaces are also observed between neighboring fibers in delignified wood-based materials and their role on mechanical properties and formability of delignified wood is discussed in detail in this thesis.
3.2. Wood – a role model for fiber reinforced composites

3.2.1. Chemical composition of wood

Wood is one of the most abundant natural materials on earth and mainly consists of biopolymers. The three main structural components are cellulose, accounting for approximately 40-50% of dry mass, hemicelluloses (25%) and lignin (25-35%). In addition, minor amounts of extractives and inorganics are present. A description of the structural components is provided in the following part.

Cellulose

Cellulose is the most abundant biomacromolecule on earth and consists of \( \beta (1-4) \) linked D-glucose units as illustrated in Figure 3.2.1-1. The chains are highly oriented and have a polymerization degree (PD) of approximately 10’000. To the current knowledge, in spruce, 24 cellulose chains arrange in nanofibrils that are stabilized by intra- and intermolecular hydrogen bonding. Nanofibrils have a diameter of around 2.5 nm and possess highly ordered crystalline domains and amorphous, domains. 

![Figure 3.2.1-1: Molecular structure of cellulose consisting of interconnected \( \beta (1-4) \) linked D-glucose units](image-url)

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Introduction

Hemicelluloses
Hemicelluloses are polysaccharide polymers with an average DP of 100-200 and are much shorter than cellulose polymers. They consist of different sugar units (glucose, mannose, galactose, xylose, arabinose and methylguluronic acid) and show a branched structure.

Galactoglucomannan is the main hemicellulose in softwood and consists of D-galactose, D-glucose, and D-mannose. Mannose and glucose form the backbone of galactoglucomannan while galactose units are attached to mannose to form a branched polymer as shown in Figure 3.2.1-2.

![Figure 3.2.1-2: Molecular structure of the hemicellulose galactoglucomannan, which is the main hemicellulose in softwood.](image)

Lignin
Lignin is a three-dimensional, heterogeneous polymer that is present in the compound middle lamella and in the matrix of the wood cell wall. It consists of aromatic phenylpropane units, which differ from each other by their degree of methoxylation. The basic structural monomer units are coumaryl alcohol, coniferyl alcohol and sinapyl alcohol and are shown in Figure 3.2.1-3. The monomers used for lignin polymerization differ between wood species. The softwood lignin (e.g. spruce) consists mainly of coniferyl alcohol units (guaiacyl lignin). During the cell wall formation process, lignin is produced by a radical polymerization.  

![Figure 3.2.1-3: Molecular structure of the lignin monomers (a) coumaryl alcohol, (b) coniferyl alcohol and (c) sinapyl alcohol.](image)
3.2.2. The hierarchical structure of wood

In the following description, the focus is laid on Norway spruce as all experiments have been conducted on this species. The biopolymers cellulose, hemicelluloses and lignin form the wood cell wall. Cellulose polymer chains cluster through inter- and intrachain hydrogen bonds to form paracrystalline microfibrils of around 2.5 nm in width,\(^{50,52,55}\) which are illustrated in Figure 3.2.2-1 in blue. These stiff reinforcing fibrils are surrounded by hemicelluloses and arrange in fibril aggregates with a diameter of 15-25 nm (Figure 3.2.2-1b).\(^{56,57}\) The two hemicelluloses glucomannan and xylan are organized differently in the cell wall. In particular, glucomannan shows a preferred orientation due to the close association to cellulose microfibrils,\(^{58}\) whereas xylan (illustrated in red) forms the link between fibril aggregates and the matrix polymer lignin\(^{58}\). Lignin, which encases the cellulose-hemicellulose clusters, also exhibits a certain alignment in relation to the fibrils.\(^{59}\) The interaction between hemicelluloses and lignin has been proposed to be of covalent nature but the exact cross-linking mechanism is still under debate.\(^{60}\)

Figure 3.2.2-1c depicts a section of the secondary S2 layer, which represents 80-86% of the cell wall.\(^{61}\) The cell wall consists of a primary layer and three secondary cell wall layers (S1-3) as illustrated in Figure 3.2.2-2a. Layers differ in microfibrillar orientation and chemical composition. The primary layer has a lower cellulose density compared to the secondary layer and exhibits a

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**Figure 3.2.2-1: Hierarchical structure of wood at the nano scale.** (a) Cellulose microfibril (blue) surrounded by the hemicellulose glucomannan (violet). (b): Cellulose fibril aggregate consisting of elementary fibrils and hemicelluloses glucomannan and xylan (red). (c) Section of a wood cell wall depicting cellulose fibril aggregates embedded in the matrix consisting of lignin (orange) and hemicelluloses.

Illustrations by Josh Binswanger, Bachelor thesis ZHdK, 2019
partially dispersed cellulose microfibril organization. In contrast, in the secondary layer, microfibril aggregates are oriented parallel to each other and spiral around the longitudinal axis with an angle deviating from the longitudinal axis, called microfibril angle (MFA). S1 and S3 possess a relatively large deviation from the longitudinal axis (high MFA) whereas a low MFA is typically observed in the S2 layer for normal adult wood. The MFA in the S2 layer varies considerably depending on cell phase (juvenile or adult) and loading condition during growth, and influences strength and elasticity of the wood tissue.

Tracheids, elongated cells, are connected through a matrix of lignin and pectin. They are unidirectionally aligned in the tree in order to provide mechanical support while simultaneously enabling water and nutrient transportation along the axis through lumina and pits. The tube-like character not only allows for transportation, but additionally results in a lightweight design at tissue level (Figure 3.2.2-2b). Alternating regions of high density (latewood) and low density (earlywood) cells are visible. So called growth rings are a result of seasonal variations, which influence the growth pattern of a tree. The tissue of softwoods (gymnosperms) as presented here for Norway spruce has a rather simple structure and consists mainly of tracheids, responsible for structural support and conduction in the axial direction, and parenchyma, responsible for storage and radial transport (Figure 3.2.2-2c).

![Hierarchical structure of wood at the micro scale.](image)

(a) Wood cell wall (tracheid) with layered structure. (b) Section of wood tissue showing latewood cells, early wood cells and bordered pits. (c) Zoomed out-section of the wood tissue.

Illustrations by Josh Binswanger, Bachelor thesis ZHdK, 2019
3.2.3. Norway spruce (Picea abies)

This species is highly abundant in northern and central Europe. Norway spruce is a softwood and consists approximately to 95% out of tracheids. Additionally, a smaller fraction of parenchyma cells are mostly located in the rays.\textsuperscript{68,69} Spruce tracheids are 2-4 mm in length with an aspect ratio (L/D) of about 100:1.

In the early part of the growth season, spruce forms earlywood consisting of thin-walled (about 2 µm single-cell wall thickness)\textsuperscript{69} tracheids. The cell wall thickness increases throughout the season until at the end of the season, thick walled latewood cells (about 10 µm cell wall thickness)\textsuperscript{69} are formed. This resulting seasonal alternating density pattern is shown in Figure 3.2.3.

\textbf{Figure 3.2.3:} Light-microscope image of a cross-section of Norway spruce (\textit{Picea abies}) showing a growth ring border.
3.2.4. Adaptation to the environment – wood heterogeneities

Wood is a natural material and therefore possesses tailored heterogeneities in the microstructure caused by adaptations to the environment. Variations on all length scales, such as the orientation of microfibrils on cell wall level or fiber alignment on tissue level, influence the overall performance of the material. On the one hand, these variations within a tree need to be taken into account when producing new materials based on wood as they can cause large variations in the final material properties. On the other hand, the concepts used by nature can inspire materials scientists to optimize man-made materials towards non-uniform loading scenarios. The mechanical self-optimization of trees was summarized by Mattheck in five theorems\textsuperscript{70} and some of them have been role model for improving technical fiber composites.\textsuperscript{71} This chapter focuses on the axiom of uniform stress, which affects the outer shape of the tree, and the alignment of fibers along force trajectories.

The structure of a tree is adapted to its natural load, but if the loading conditions change, a tree is able to adapt to the new conditions by the so-called adaptive growth. This allows trees to optimize their outer shape and to fulfill the axiom of uniform stress, which leads to minimized internal stress concentrations.\textsuperscript{70,72} For example, when a tree detects a local increase in stress, e.g. around a tree branch hole, the cambium adapts the growth rates and wood formation is locally enhanced to redistribute stress concentrations\textsuperscript{73,74} as shown exemplarily around a tree branch knot in Figure 3.2.4a. The adaptation of geometry influences the growth ring width and therefore the density,\textsuperscript{49} which means that adaptive growth generally goes along with changes in material properties. Trees can additionally change their internal architecture for example by adjusting the orientation of structural components. They adapt fiber alignment in agreement with the force flow in the component in order to minimize critical shear stresses.\textsuperscript{70} A spindle-type run of fibers around a circular hole is observed around wood rays but also on tissue level around tree-branch attachments as shown in Figure 3.2.4b to minimize notch stresses.\textsuperscript{70,75}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure3.2.4.png}
\caption{(a) Tree branch hole with enhanced wood formation\textsuperscript{74} and (b) tree branch attachment showing fiber alignment adaptation.}
\end{figure}
3.3. Materials based on delignified wood

3.3.1. Bottom-up approaches

Bottom-up approaches comprise assembly processes of components into a desired microstructures. Components are often obtained by disintegration of the base material (e.g. wood) into smaller pieces such as fibers or fibrils. The use of cellulose fibers as reinforcement in composites has increased over the last few years, mainly due to their natural abundance, high specific properties, recyclability and low cost. Wood fibers from trees mainly find application in paper, cardboard and fiber-board products. Fabrics for structural components, however, are produced out of plant fibers such as hemp or flax. This is mainly because the assembly into oriented structures is easier for long plant fibers compared to short wood fibers. The variability of mechanical properties arising from defects or seasonal variations is still a big issue for natural fiber composites in general.

Nanofibrillated cellulose (NFC)

One strategy to minimize inhomogeneities is the disintegration of the natural fiber into nano-scale building blocks followed by re-assembly. The number of publications on nanocellulosic materials increased over the last 20 years. These materials are particularly interesting as reinforcing component due to their high axial modulus, their large surface area and their high amount of reaction sites, which offer good functionalizability. NFC-based materials are biodegradable, and show strong fiber-fiber interaction, which led to the development of nanocellulose films, foams, or cellulose nanofibril-reinforced polymer composites.

Alignment of nanocellulosic building blocks

It is very challenging to fully profit from nanocellulosic fiber’s high mechanical performance after assembly into macroscopic materials. To make full use of the mechanical potential of reinforcing fibrils, alignment is crucial but very challenging. Alignment of building blocks has been obtained for example by drawing, by shear induced alignment in 3-D printing or by flow-assisted organization into macroscale fibers. Still, it is questionable whether an energy intense disassembly process followed by elaborate assembly-processing is the method of choice when it comes to the production of larger-scale structural components.
3.3.2. Top-down approaches

Due to the energy intense nature of disassembly processes and challenges with assembling, the interest in top-down approaches as an alternative to bottom-up manufacturing techniques is steadily growing. In recent years, a direct use of the wood inherent cellulose scaffolds based on partial or complete delignification of wood has been investigated. This method has the strong advantage of retaining the alignment of cellulose during the process, eliminating energy intense disassembly and critical assembly steps. New functional or structural materials are derived directly from the wood scaffold. This chapter aims to give an overview about current delignification techniques and material development based on delignified wood.

Delignification procedures

Delignification in the pulp and paper industry

Delignification is a well-established process in the pulp and paper industry for separating lignocellulosic materials into lignin and cellulose. Commercial industrial pulping processes comprise thermomechanical methods, chemical pulping, or a combination of both, known as semi-chemical pulping.\(^87\) Thermomechanical methods soften the lignin prior to mechanical grinding but lignin remains in the fibers. The process results in rigid, lignified fibers that show relatively poor bonding strength. Semichemical pulping uses pretreatments that partly remove hemicelluloses and lignin for eased mechanical defibration.\(^87\) Chemicals used include sodium hydroxide (NaOH), sodium sulfide (Na\(_2\)S) or sodium carbonate (Na\(_2\)CO\(_3\)) at mild conditions.\(^88\) Chemical pulping is conducted at harsher conditions and comprises the complete removal of lignin and hemicellulose. It results in fibers with a higher flexibility but reduces the fiber yield.\(^87\) The most common pulping process is the kraft process, also known as sulfate process, which combines cooking in a mixture of water, sodium hydroxide (NaOH) and sodium sulfide (Na\(_2\)S) with mechanical processing steps.\(^89\) Kraft pulp consists of completely delignified fibers with a straight shape and a low amount of defects and thus results in a very high paper quality.\(^87\) Various other delignification strategies exist and all of them usually comprise the addition of bases or acids such as NaOH and H\(_2\)SO\(_4\) but also other reactants including H\(_2\)O\(_2\), organosolv (Lewis acids, FeCl\(_3\), (Al)\(_2\)SO\(_4\) in aqueous alcohols) or phenol are known to promote hydrolysis.\(^90,91\)
Structure-retaining delignification

In principle, all standard delignification methods that are used for pulp and paper production can be used for the production of structure-retained delignified wood. However, unlike in common delignification treatments, which are aiming for a disintegration into single fibers, structure-retaining delignification keeps the cellulose arrangement and hierarchical architecture of native wood.\(^{92}\) In structure-retaining delignification, matrix components are partially or completely removed and make the wood inherent cellulose scaffold more accessible for functionalization. Scaffolds can further be chemically modified to provide materials with new functionalities or densified to obtain cellulose materials with enhanced mechanical properties. Delignification methods and degrees need to be selected depending on the targeted purpose of the obtained scaffold and some methods that have already been reported in former works on delignified wood are described in the following.

A combination of \(\text{NaClO}_2\) and \(\text{NaOH}\) under mild conditions was used by Yano et al. 2001 to remove matrix substances as pretreatment prior to polymer infiltration.\(^{10}\) In this approach, \(\text{NaClO}_2\) partly delignifies the wood scaffold and the subsequent \(\text{NaOH}\) treatment removes hemicelluloses. Performed at mild conditions, this method proved to be a promising way to remove matrix substances without affecting the strength of microfibrils and was adapted by Li et al 2016 for the manufacturing of transparent wood.\(^{13}\)

Song et al. 2018 performed a structure-retaining partial lignin and hemicellulose removal via a boiling process in an aqueous mixture of \(\text{NaOH}\) and \(\text{Na}_2\text{SO}_3\) to produce densified delignified wood with high strength.\(^{93}\) Sulfonation of lignin enables lignin to better dissolve in alkaline solution and therefore speeds up the reaction time. The same delignification method was used to produce flexible wood membranes\(^{94}\) and for the production of transparent wood by Zhu et al. 2016. However, an additional bleaching treatment in \(\text{H}_2\text{O}_2\) had to be performed prior matrix infiltration for obtaining transparency.\(^{95}\)

Segmehl et al. recently compared acidic bleaching by a hydrogen peroxide/acetic acid treatment and soda pulping with sodium hydroxide (10 wt %).\(^{91,92,96}\) Acidic bleaching was found to be an appropriate method for bulk wood delignification as the reaction is initiated at elevated temperature and therefore allows an infiltration of the solution into the wood tissue at RT prior activation. A treatment at 80 °C led to completely white cellulose scaffolds with low dimensional
stability in wet state. The second method, soda pulping, effected mainly the middle lamella region while the aromatic content in the secondary cell wall region did not decrease.92

**Materials based on structure-retaining delignification**

**Functional materials**

Partial or complete removal of lignin influences the porosity of wood on cell wall and tissue level and is therefore a highly beneficial method to improve penetrability and functionalizability for novel hybrid materials. The scaffolds inherent interconnected porous path consisting of lumina and pits and the porous cell walls can be infiltrated with functional materials or matrix components. The infiltration or functionalization of lumina and pits is illustrated in *Figure 3.3.2.-1c*. If cell wall pores are large enough, respectively the functionalizing agent is small enough, cell walls are additionally functionalized as illustrated in *Figure 3.3.2.-1e*. Such a combination of lumina and cell wall functionalization represents the infiltration of MMA monomers into delignified wood cell wall and lumen pore space, which lead to the fabrication of transparent wood.102 In contrast, *Figure 3.3.2.-1.d* illustrates cell wall modification, in which only cell wall pores but not the lumina are functionalized. An example for cell wall modification has been shown by Fu et al. 2017, where clay impregnation into the cell walls of delignified balsa wood followed by freeze drying lead to improved fire-retardancy.100 By a combined infiltration of magnetic Fe3O4 nanoparticles and index-matching methyl methacrylate into delignified wood, even a combination of transparency and magnetism was achieved.103

![Figure 3.3.2-1](image)

*Figure 3.3.2-1*: (a) native wood, (b) delignified wood, (c) infiltration of lumina with e.g. a polymer, (d) cell wall functionalization by infiltrating the porous cell walls by e.g. clay, epoxy or magnetic nanoparticles, (e) combination of lumina and cell wall functionalization.
A novel potential application of wood-based materials are wood filters or membranes due to the intrinsic anisotropic open porous path of the material.\textsuperscript{104,105} Structure-retaining delignification was proposed to help improving the performance of filters and membranes, due to the larger surface area and better functionalizability due to the higher porosity of the modified scaffold.\textsuperscript{101} Fu et al. 2018 reported the fabrication of strong, mesoporous and hydrophobic biocomposites for the selective separation of oil/water mixtures by using a functionalized delignified wood scaffold. The hydrophilic porous delignified wood was impregnated with epoxy resulting in a hydrophobic oleophilic wood scaffold that was able to absorb oil under water or from the water surface.\textsuperscript{11} In another work, flow conductivity of delignified freeze-dried wood was utilized in oil-absorbing anisotropic wood sponges. The spring like structure of the wood sponge allowed the removal of oil after use by simple squeezing and the intact cellulose scaffold allowed a re-use of the sponge.\textsuperscript{106}

The spatial arrangement of functionalizing components can potentially be tailored by adjusting the delignification degree and by the choice of the wood species, as these parameters influence the porosity of the cellulose scaffold.\textsuperscript{9,99,101} Softwoods with an alternating latewood-earlywood pattern for example show bands of different strength and flow conductivity,\textsuperscript{9} which can lead to desired alterations in functional or mechanical properties. Flow-through devices for filter or membrane applications, however, are often based on hardwoods. Their long pipes for water transportation in the wood tissue, so-called vessels, can be better utilized for the directed flow.\textsuperscript{9}

**High-strength materials**

Structure-retaining delignification has been utilized to fabricate high-strength wood-based materials. The structural support of these materials is provided by the delignified wood cell walls. Therefore, increasing the cell wall fraction and with that the volume content of the reinforcing phase, e.g. through densification, increases mechanical properties. Structure-retaining delignification combined with densification increases mechanical performance of transparent films\textsuperscript{107} and of transparent plywood.\textsuperscript{12} Transparent plywood with a maximum FVC of 12\% showed 62 MPa in strength and 4.3 GPa in stiffness.\textsuperscript{12}

For specifically optimizing mechanical properties, the FVC need to be increased to even higher values. Yano et al. densified birch wood samples, which were preselected with sound velocity measurements before partial delignification and infiltration with a phenol formaldehyde (PF)-resin, and obtained very strong and stiff wood-based composites\textsuperscript{10,108} by strong densification up to a density of 1400 kg m\textsuperscript{-3}. With this technique, bending strength and stiffness of 670 MPa and
62 GPa were obtained. Figure 3.3.2-2c shows the general manufacturing steps for such a resin-infiltrated high-performance composites.

Song et al. produced resin-free high-performance materials as illustrated in Figure 3.3.2-2b by hot densification of partially delignified wood. The bonding capacity of the remaining lignin combined with the inherent unidirectional cellulose alignment contributed to the high bending strength of approximately 600 MPa, stiffness of 50 GPa and high toughness.

Samples prepared by Yano and Song et al. both possess a cellulose fiber volume content above the theoretical maximum value derived for man-made composites. This is possible due to the deformability of delignified wood scaffolds and different stress-transfer mechanisms relying on the fiber-fiber interface instead of the fiber-matrix interface. Within the framework of this thesis, these concepts is further explored for the development of novel structural wood-based materials.

Figure 3.3.2-2: Overview of processing steps to obtain structure-retained delignified wood based materials. (a) Native wood, (b) (partially) delignified wood and high-performance cellulose-materials after densification, (c) polymer-infiltrated delignified wood and high-performance cellulose-polymer composites after densification.
4 Publications

This cumulative thesis is based on the following four first-author papers

First author papers:


**Contributions:**
M.F.: performed experiments, analyzed data, and cowrote the manuscript; D.W.: performed experiments and analyzed data; J.S.: performed experiments and analyzed data; K.C.: performed experiments and analyzed data; T.K.: analyzed data and cowrote the manuscript; I.B.: designed the study, analyzed data, and cowrote the manuscript. All authors discussed the results and commented on the manuscript.


**Contributions:**
M.F. and T.K. conceived the study. M.F., G.B., M.A.-V., M.Z., Y.W., K.T. and A.M.H. performed experiments and analyzed data. M.F., K.M., T.K., and I.B. co-wrote the manuscript. All authors discussed the results and commented on the manuscript.


**Contributions:**
M.F., M.Z., C.D., E.F. and E.T. performed experiments and analyzed data. M.F., T.K., and I.B. co-wrote the manuscript. All authors discussed the results and commented on the manuscript.

Contributions:
MF: Designed the study, performed experiments, analyzed data and co-wrote the manuscript; LS: Performed experiments and analyzed data; KM: Designed experiments, Analyzed data and co-wrote the manuscript; TK: Analyzed data and co-wrote the manuscript; IB: Analyzed data and co-wrote the manuscript.

Other publications:


Patent:

4.1. Delignified and Densified Cellulose Bulk Materials with Excellent Tensile Properties for Sustainable Engineering

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Abstract

Today’s materials research aims at excellent mechanical performance in combination with advanced functionality. In this regard great progress has been made in tailoring materials by assembly processes in bottom-up approaches. In the field of wood-derived materials, nanocellulose research has gained increasing attention and materials with advanced properties were developed. However, there are still unresolved issues concerning upscaling for large scale applications. Alternatively, the sophisticated hierarchical scaffold of wood can be utilized in a top-down approach to upscale functionalization and one can profit at the same time from its renewable nature, CO\textsubscript{2} storing capacity, light weight and good mechanical performance. Nevertheless, for bulk wood materials a wider multi-purpose industrial use is so far impeded by concerns regarding durability, natural heterogeneity as well as limitations in terms of functionalization, processing and shaping. Here we present a novel cellulose bulk material concept, based on delignification and densification of wood resulting in a high performance material. A delignification process using hydrogen peroxide and acetic acid was optimized to delignify entire bulk wooden blocks and to retain the highly beneficial structural directionality of wood. In a subsequent step, these cellulosic blocks were densified in a process combining compression and lateral shear in order to gain a very compact cellulosic material with entangled fibres while retaining unidirectional fibre orientation. The cellulose bulk materials obtained by different densification protocols were structurally, chemically and mechanically characterized revealing superior tensile properties compared to native wood. Furthermore, after delignification
the cellulose bulk material can be easily formed into different shapes and the delignification facilitates functionalization of the bio-scaffold.

**Introduction**

In producing wood, trees provide an excellent renewable biomaterial comprising high specific strength and stiffness.\(^1\)\(^-\)\(^2\) The hierarchical structure and fibrous architecture with aligned fibers, which are composed of rigid cell walls that consist of high-strength cellulose fibrils embedded in a pliant matrix of hemicelluloses and lignin, has been a great source of inspiration for the design of engineered composites.\(^3\)\(^-\)\(^4\) In recent years, there has been an increasing number of publications that report on the functionalization of the sophisticated wood structure to develop materials with novel properties,\(^5\)\(^-\)\(^6\) including transparency,\(^7\)\(^-\)\(^8\) magnetism\(^9\)\(^-\)\(^10\), electrical properties,\(^11\)\(^-\)\(^13\) stimuli-responsiveness\(^14\) as well as for filtration and oil-water separation purposes.\(^15\)\(^-\)\(^16\) These are so far mainly fundamental works that show the principle approach and the application potential, but for a broader utilization and implementation of such wood materials in high-end applications certain limitations need to be overcome. These mainly arise from the heterogeneity of the wood substrate, causing a low reliability in terms of material properties and little control of the efficacy of the functionalization.

Since wood is the product of a natural growth process influenced by environmental factors, its tissue structure, and hence density can vary substantially within a species and even within a trunk of an individual tree. Furthermore, mechanical adaptations during the life of the tree at the tissue and fiber level or the presence of natural features such as knots result in additional variability, which leads to concerns regarding the reliability of wood, respectively predictability in high-performance applications. A prominent process to achieve a higher homogeneity of wood and to preserve the structural directionality is densification, since the density is one of the dominating factors dictating mechanical properties.\(^17\) Bulk wood samples can be compressed to reach high and homogenous density levels accompanied by significant mechanical property improvements.\(^18\)

Partial delignification of wood and adding of moisture facilitates densification processes\(^19\) and infiltration with resins can result in strong natural fibre-reinforced composites.\(^19\)\(^-\)\(^20\) A strong compression of delignified wooden films was shown to result in a pronounced anisotropy with high longitudinal tensile strength.\(^8\)

Moreover, it is difficult to functionalize the compact wood cell wall. Thus only a very limited number of bulk wood modifications have been successfully commercialized,\(^21\)\(^-\)\(^22\) while with many
other approaches, property improvements could only be achieved by rather complex chemistries.\textsuperscript{23} Hence, in the last two decades a strong focus has been laid on the decomposition of wood down to the nanoscale, enabling the use of delignified cellulosic material including nanofibrillated cellulose and cellulose nanocrystals. The utilization of this type of cellulose materials further allows for the application of simple and versatile functionalization approaches.\textsuperscript{24-27, 28, 29} However, so far it is a great challenge to transfer the mechanical performance of the individual units to the bulk composite material as fibre re-orientation and assembly are difficult to achieve. Although great progress was made towards nanocellulose re-orientation in micro-fluidic devices\textsuperscript{30} and in 3D- or even 4D-printing processes\textsuperscript{31, 32} it remains a challenge to achieve nanocellulose-based materials with excellent mechanical performance at the macroscale.

![Figure 1. Delignification of native wood (a, d, g) results in a white cellulose scaffold (b, e). The matrix lignin is removed between the cells (e) and in the cell wall, which results in a flexible cell wall (h). Densification of the delignified cellulose scaffold (c) results in a homogenous folding of the earlywood cells (f) and in wrinkling of latewood cells (i).](image)

Here we present a novel cellulose bulk material, which was obtained by a subsequent combination of delignification and densification while retaining the beneficial hierarchical structure and fiber directionality of wood.\textsuperscript{33} The obtained cellulose material was structurally, chemically and mechanically characterized at different length scales as illustrated in Figure 1. For mechanical
analysis at the macroscopic level tensile tests were conducted and the influence of densification on the folding behavior of earlywood cells was examined by light microscopy and SEM at the tissue level. Structural changes at the cell wall level due to delignification and densification were studied on latewood cells by AFM measurements.

**Experimental section**

*Delignification procedure*

Norway spruce samples were cut to the dimensions 100 x 10 x 20 mm³ (longitudinal x radial x tangential). Eight samples per variant were cut from the same height in the trunk from matched positions in order to obtain similar growth ring patterns. The pieces were stored at 20 °C/65 % rel. humidity before treatment. Afterwards, the wood samples were placed into a beaker on top of a metal-grid sample holder. An equal-volume mixture of hydrogen peroxide solution (35 wt-%, Acros Organics) and glacial acetic acid (Fisher Chemicals) was prepared. The bulk wood pieces were infiltrated over night at room temperature under stirring. The solution was then heated and the pieces were delignified for 6 h at 80 °C. Infiltration (overnight) and delignification (6 h, 80 °C) processes were repeated once with a fresh H₂O₂-HAc solution. After delignification, the samples were washed in water with an exchange of the water for five times daily until the pH value of the water was above 4.5. To retain the structural integrity of the samples, they were confined in a metal-grid clamp during the washing step. After washing, samples were conditioned until a constant mass was obtained.

*Weight loss, volume loss, density*

Mass and volume of the samples were measured before and after the delignification step and after densification. Measurements were conducted after conditioning the samples at 65% relative humidity. Comparing mass and volume of native wood to the values obtained for the delignified cellulose scaffolds allowed for calculating the weight and volume loss and the change in density caused by the delignification.

*Fourier transform infrared (FTIR) spectroscopy*

Thin slices of delignified wood pieces were analyzed with a FT-IR spectrometer (Bruker Tensor 27). Spectra were baseline corrected (concave rubberband) and normalized (min/max) in the OPUS software and plotted in Origin 2016.
Densification procedure

Delignified bulk wood pieces were densified in radial direction using a universal testing machine (Zwick Roell, 100 kN load cell) in compression mode. A punch was pressed stepwise (1 mm compression, 15 s waiting time) into the mold containing the specimen (100 x 20 mm²). Prior to densification the delignified bulk wood pieces were either conditioned at 20°C and 65% relative humidity or at 20°C and 95% relative humidity. During the densification process the specimens were compressed from an initial thickness of 10 mm to a final thickness of 3.5 mm for low force (LF) densification and of 2.5 mm for high force (HF) densification (see Figure S1 for the force and displacement regime of the latter). For both moisture contents and force conditions an additional lateral movement of the punch was applied during compression. This lateral movement was induced by an air compressor gun (2 bar) connected to the punch. After densification, the densified pieces were conditioned at 20°C/65 % relative humidity. For each variant, seven samples were used for tensile testing and the remaining sample was used for characterization by light microscopy and SEM. As an additional reference, native wood was densified resulting in a thickness of the specimens of approximately 5.5 mm.

Tensile testing

The outer parts of the edges were cut and the specimens were grinded (sandpaper grit size 200 & 600) to achieve regular cross-sections prior to testing of the tensile properties of the specimens in a Zwick Roell (100 kN load cell). The distance between the clamps was determined with 36 mm and the displacement was measured with a video extensometer, detecting two indicator strips placed on the specimen surface with an initial distance of 25 mm. The tests were conducted at 20°C and 65% relative humidity at a speed of 5 mm/min until a 30 % force drop after the maximal force (Fmax) had been reached. The tensile strength and the tensile modulus were calculated based on Fmax and on the slope between 10 % - 30 % of Fmax, respectively. The work until fracture was calculated as the integral of the force-distance curve until failure of the sample.

Microtome & Ultramicrotome Cutting

The samples surfaces characterized by light microscopy (Olympus BX51) and AFM (JPK Instruments AG) were prepared using a rotary microtome (Leica Ultracut, Germany). Samples for AFM measurements were additionally cut using an ultramicrotome (Reichert Jung-Ultracut) with a diamond knife (Diatome).
**Atomic force microscopy (AFM)**

AFM imaging was performed using a NanoWizard 4 (JPK Instruments AG) in the Quantitative Imaging mode (QI) at 20 °C and 65% relative humidity. The resolution was set to 256 x 256 pixels and the scan size was 20 x 20 µm. A non-contact cantilever (NCHR, NanoWorld, resonance frequency 320 kHz) with a silicon probe was used. The setpoint was set to 60 nN, the z-length to 100 nm and the pixel time was set to 12 ms. Calibration of the cantilever was done with the thermal noise method. The generated images were processed with the JPK image processing software (JPK Instruments AG).

**Scanning electron microscopy (SEM)**

Delignified and densified wood pieces were coated with a sputter coater (CCU-010, Safematic, Switzerland). A Pt-Pd (80/20) coating of ~6 nm thickness was applied. For the measurements a Hitachi SU5000 was used.

**Results and discussion**

In a first step, spruce bulk wood was delignified with an equal-volume mixture of hydrogen peroxide and acetic acid, removing all lignin and parts of the hemicelluloses as can be seen in terms of changes of respective peaks in the IR spectra (Figure 2).

![Figure 2. FTIR spectra of native and delignified spruce wood samples in the spectral range from 1800 to 900 cm⁻¹. The absence of characteristic lignin peaks at 1593 cm⁻¹, 1460 cm⁻¹, 1509 cm⁻¹ (aromatic skeletal vibration) and 1264 cm⁻¹ (guaiacyl ring breathing with CO stretching) confirm a complete removal of lignin. Changes in the area from 1200 to 1000 cm⁻¹ mainly arise from the reduction of hemicelluloses.](image-url)
The complete lignin removal can be directly concluded from the entire absence of the lignin specific IR bands, whereas changes in hemicelluloses are obvious in the spectral range from 1000 - 1200 cm⁻¹, but a detailed quantification of the content is limited because of the partial overlap with cellulose bands. However, the loss of hemicelluloses can be estimated by taking the total mass loss of 40% during delignification into account (Fig S2). According to literature values, spruce wood consists of ~31% hemicelluloses and ~28% lignin,36 which results in a reduction of hemicellulose content of around one-third. Moreover, the densification process does not only result in a mass reduction but also in a volume loss of more than 20% (Figure 3b, and S2). It can be assumed that this leads in total to a higher porosity of the specimens, as the entire density is reduced from 440 kg/m³ in the native state to 330 kg/m³ in the delignified state, respectively.

In a subsequent step, the cellulose bulk material was densified to a defined thickness, while simultaneously applying lateral shear.33 Two different densification levels termed low force densification and high force densification were applied and distinguished on the basis of the targeted and achieved sample height after the densification. Furthermore, the densification was conducted at two different equilibrium moisture contents adjusted at 65% relative humidity and 95% relative humidity, respectively. Figure 3 shows the forces that were applied to achieve the targeted specimen heights and the resulting densities in all tested sample categories.

![Figure 3](image.png)

**Figure 3.** Densification force (a) and resulting densities (b) of all sample categories. Higher humidity in the delignified scaffold results in lower densification forces and higher densities.

The delignification process facilitates cell collapse during densification,19 most probably due to a reduction of the transverse rigidity of the cell walls. Delignified cells were smoothly compressed
and almost no cracks could be observed in the cell walls, whereas densified native (lignified) bulk wood showed extensive cell wall cracking, in particular in the latewood region (Fig. S3). After delignification and low force densification a cell folding of the thin-walled earlywood cells could be observed (Fig. 4). Highly compressed latewood regions were only found after high force densification.

![Figure 4. SEM images of earlywood (a,b,c) and latewood (d,e,f) cell walls before densification a,d) and after low force densification (b,e) and high force densification (c,f) with applying lateral shear.](image)

The combination of compressive and lateral shear forces affected the structural organization of the cellulose material at two hierarchical levels. Light microscopy images showing the cell and tissue level, reveal in agreement with the SEM investigations, that a densification at low-force after equilibration at 65 % relative humidity, resulted in a collapse of the earlywood cells, but that the more compact latewood cells were not fully compressed. A zoom in the earlywood zone reveals a very regular transverse folding of cells at the tissue level (Figure 5b), whereas for specimens that were densified without applying lateral shear, a more irregular and uneven cell collapse was found (Figure 5e). Additionally, the shear affected the mode of cell wall deformation during the process. AFM studies showed that the thick cell walls of samples that were densified without lateral shear were more wrinkled and distorted while the samples that were densified with lateral shear possessed more smoothly compressed cell walls (Figure 5c,f).
Figure 5. Delignified specimens densified at low-force after equilibration at 65 % relative humidity with and without lateral shear (a,d). A zoom into earlywood region by light microscopy (b,e) shows that folding of earlywood cells is more homogenous, when lateral shear is applied during densification. AFM images of densified latewood cells with shear (c) and without shear (f) during densification reveal the smoothening effect of shearing on the cell wall level.

Tensile tests of the bulk cellulose specimens show that remarkable material properties can be achieved. It is important to emphasize that the tested samples were totally resin-free and therefore only the bond forces between the aligned cells and cellulose fibrils were decisive. The different levels of densification and relative humidity affected the obtained mechanical properties (Figure 6).
Figure 6. Mechanical characterisation of the reference samples (native, native densified) and of shear assisted densified cellulose scaffolds conditioned at 20°C and 65% relative humidity by longitudinal tensile tests. a, Representative stress-strain curves for each treatment. b, Work until fracture (b: n=8 for native; n=5 for native densified, LF/65%, LF/95%; n=7 for HF/65%, n=6 for HF/95%). c, Elastic modulus. d, Strength. e, Specific elastic modulus. f, Specific strength (c-f: n=8 for native; n=6 for native densified; n=5 for LF/65%; n=7 for LF/95%, HF/65%, HF/95%).

The stress-strain curves of representative tests show the severe impact of the densification treatment on the mechanical behavior (Fig. 6a). A comparison of the elastic moduli of the samples indicated that compression with higher forces results in higher values and that higher humidity levels are favorable and hence superior properties are achieved by a strong densification of samples conditioned at high relative humidity (95% RH) (Figure 6c). A very similar trend was obtained for the tensile strength, again showing that strong densification is superior to light
densification and that a compression at high humidity levels outperforms compression at low humidity levels (Figure 6d). Remarkably, in comparison to native spruce (Young’s modulus ~13 GPa, tensile strength ~80 MPa) an up to three times higher stiffness could be achieved and also the tensile strength was succeeded by a factor of three for the highly densified samples. Contrary the application of the same densification protocol to native spruce resulted in a loss in elastic modulus and a moderate increase in strength, underlining the crucial relevance of the delignification for the loss of transverse cell wall rigidity in this particular process. Eliminating the influence of density differences by calculating the specific elastic moduli and the specific tensile strengths (Fig 6e,f) shows that material improvements can particularly be achieved for specimens densified at high humidity and high compression forces.

Furthermore, the work until fracture of the cellulose materials was calculated on the basis of the tensile tests (Fig 6b). These calculations could only consider the mechanical response until a strain at which the two indicator strips on the specimen surface for displacement detection were misaligned due to fracture events. However, the obtained results indicate that the cellulose materials compressed with high force reach higher values compared to the specimens compressed with low force. The densified native wood specimens reached work until fracture values similar to the delignified specimens compressed at high force, but their elastic modulus was much lower. This interrelation can be illustrated by comparing the sample categories on the basis of elastic moduli and work until fracture (Fig. 7).

![Figure 7. Comparison of elastic modulus and work until fracture of the different categories of cellulose material. All error bars represent the standard deviation (n=8 for native; n=5 for native densified, LF/65%, LF/95%; n=7 for HF/65%, n=6 for HF/95%).]
The comparison in Figure 7 shows that the applied delignification and densification protocols allow for producing cellulose bulk materials with a highly desired material property combination of improved stiffness and toughness. Although, the strain to fracture was comparably low for all tested samples, in particular the specimens that were densified with high force at high moisture content show superior properties for both mechanical parameters. This combination can be found in several biological systems (e.g. bone), but a transfer to engineering materials is challenging.

Besides the improved mechanical performance, the material concept has the major advantage that the delignified samples can be easily deformed and elements with different shapes and complex geometries can be produced by non-cutting processes (Figure 8).

**Figure 8.** Elements of different shapes and geometries with perfectly aligned fibers. a, curved. b, twisted. c, graded. d, branched. The structures can be manufactured by simply forming the cellulose scaffold in wet state.

Remarkably, even for high curvatures the fibers are kept perfectly oriented related to the distribution of forces and no fibers need to be cut as known to be common in current wood processing techniques. This makes curved or twisted structures (Figure 8) more mechanically robust and vast applicable as load-bearing elements. Further, the material’s flexibility also allows for easily designing connections that fully respect fiber alignment, as it is known for many biological role models, for instance in tree or cacti branching. Connecting fibrous elements has ever been a challenge in fiber composite design, as an interweaving of fibers is needed to
sufficiently transfer forces between two connected elements. Moreover, the level of densification can be easily varied within individual elements, for the design of composites with gradual alterations in height, density and stiffness.

The here presented cellulose bulk materials have been fabricated without the addition of an adhesive system. However, considering the effect of delignification, an eased insertion of thermoplastics or thermosets into the cellulose scaffolds can be expected. Such an insertion would most likely provide higher strength and toughness. Although the individual crystalline cellulose unit possesses a very high stiffness and strength and also single plant fibers from hemp, flax or bamboo are known for exceptional tensile properties, it remains a challenge to transfer these performances to the macroscopic composites. A high tensile strength of 350 MPa was achieved for 80 μm thick wood films, but there are only a few examples, like bamboo-epoxy composites or wood polymer composites that have reached superior mechanical properties at the macroscale. Natural fibre composites that are based on embedding single fibres in a matrix have by far lower stiffnesses and strengths, which clearly shows the advantage in retaining the natural fibre assembly for the production of bio-based engineering composites. Hence, the presented bulk cellulose composites represent an important step forward towards high performance load bearing applications based on renewable lignocellulosic materials. However, further investigations need to be conducted with different wood species, on resin impregnation, and on densification with different shear levels for gaining further insight into the specific impact and an optimization of the wood composites.

**Conclusion**

A cellulose bulk material was developed in a stepwise process of delignification and subsequent shear assisted densification, which resulted in compact composites with a specific fibre folding pattern. Even without adding a matrix system the obtained mechanical properties were superior to wood and many other natural fibre-reinforced composites. For the strongly densified 95% RH samples an average elastic modulus of ~40 GPa and a tensile strength of ~270 MPa were reached. This is accompanied by an improved work until fracture compared to wood, which in combination with the high stiffness is highly desired. Furthermore, the composites can be easily pre-formed to different shapes and the delignification facilitates functionalization treatments. Based on the mechanical performances obtained and in view of their origin from a highly abundant and
renewable resource, these sustainable cellulose materials are predestined for novel fibre-reinforced biocomposites.

Authors’ contributions
MF: Performed experiments, analyzed data and co-wrote the manuscript; DW: Performed experiments and analyzed data; JS: Performed experiments and analyzed data; KC: Performed experiments and analyzed data; TK: Analyzed data and co-wrote the manuscript; IB: Designed the study, analyzed data and co-wrote the manuscript. All authors discussed the results and commented on the manuscript.

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Competing interests
The authors declare no competing financial interest.

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4.2. Tunable Wood by Reversible Interlocking and Bioinspired Mechanical Gradients

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Abstract

Elegant design principles in biological materials such as stiffness gradients or sophisticated interfaces provide ingenious solutions for an efficient improvement of their mechanical properties. When materials such as wood are directly used in high-performance applications, one cannot entirely profit of these optimizations because stiffness alterations and fiber alignment of the natural material are not designed for the desired application. In this work, wood is turned into a versatile engineering material by incorporating mechanical gradients and by locally adapting the fiber alignment, using a shaping mechanism enabled by reversible interlocks between wood cells. Delignification of the renewable resource wood, a subsequent topographic stacking of the cellulosic scaffolds, and a final densification allows fabrication of desired three-dimensional shapes with tunable fiber architecture. Additionally, prior functionalization of the cellulose scaffolds allows for obtaining tunable functionality combined with mechanical gradients. Locally controllable elastic moduli between 5 GPa and 35 GPa are obtained, inspired by the ability of trees to tailor their macro- and micro-structure. The versatility of this approach has significant relevance in the emerging field of high-performance materials from renewable resources.
Introduction

Biological materials are able to optimize their structure\cite{1, 2} and chemical composition\cite{3} to adapt to changing environmental conditions.\cite{4} They can cope with external loading conditions by locally altering their stiffness, for example by adjusting the density,\cite{2} the alignment of stiff reinforcing building blocks,\cite{5, 6} the chemical constituents,\cite{3} or by interface design strategies.\cite{7} Interfaces in biological materials can rely on both, structure or chemistry. In the example of wood, the interface properties between stiff cellulose fibrils and the soft matrix are determined by a multitude of weak chemical bonds,\cite{8} whereas in the beak of the red-bellied woodpecker\cite{9} or in the osteoderms of a leatherback sea turtle shell, jigsaw-like or sutured patterned interfaces lead to stress transfer or enable deformation.\cite{10}

The efficient design of biological materials comprising hierarchical structuring, gradients, functionality and specific interface structures has been role model for the development of bioinspired materials.\cite{11} Although various bottom-up approaches have shown the potential of assembling building blocks to transfer bioinspired design principles into synthetic materials,\cite{12} it still remains challenging to reach the structural complexity of biological materials and to fabricate them in an environmentally-friendly and scalable manner.\cite{4} In contrast, when biological materials such as wood are used in top-down approaches, their hierarchical structure can be retained and modified.\cite{13} A top-down wood modification approach gaining increasing attention is the delignification of wood by a structure-retaining treatment, which leads to formability and enhanced mechanical performance upon densification of the material.\cite{14, 15} However, the full potential of cellulose scaffolds has not yet been exploited. Beyond rather simple densification treatments, the delignified wood could be processed further to obtain a novel material combining adaptation of shape, mechanical gradients and tunable functionality.

Here we present a versatile strategy to develop smart materials of renewable nature and enhanced performance based on wood by implementing bioinspired structural, chemical and mechanical gradients as well as adaptive shape. We tune mechanical properties and locally optimize the material for external loading conditions in a simple, scalable and predictable fashion. A moisture-triggered formability is induced by removing the lignin interface between cell walls, which enables shear deformation of the material in wet state. This type of shaping results in an optimized fiber orientation, mimicking the adaptive fiber alignment in trees.\cite{6, 16} Densification and drying causes close contact between fibers and creates strong interfaces based on mechanical
interlocking and hydrogen bonding. By locally varying the degree of densification, we show the ability to spatially tune the mechanical and functional properties. A superhydrophobic surface treatment of the desired geometry finally freezes the obtained architecture. With our approach biological design principles, such as density gradients, fiber alignment and reversible interlocking mechanisms, are incorporated into the hierarchical wood material.

**Results and discussion**

**Figure 1.** Shaping mechanism of delignified wood using moisture induced reversible interlocks. a) Delignified wood samples in the locked, intermediate, morphing and re-locked (after reshaping) state. b) Scheme of a longitudinal section of delignified wood in the four states, illustrating the swelling of delignified wood fibers (black) by water (blue). c) Scheme of a cross-section and (d) AFM images of the cell corner.
Structure-retaining delignification of wood results in the removal of the matrix lignin, which acts as an adhesive between the wood fibers (tracheids). Remarkably, delignified wood is still mechanically stable in its dry state at 20°C/65% RH with a water content of 11.1%. The stability is due to mechanical interlocking in the cell corner regions, which leads to connected neighboring fibers and compensates for the removed lignin matrix. In this state, delignified wood can be used as a structural material. In contrast, in the water-saturated morphing state (water content of 435.4%), water disengages the interlocks by swelling the material and creating space between the tracheids, which leads to a low shear modulus, making the wood shapeable (Figure 1).

To investigate the water-triggered shaping of the cellulosic material on a macroscopic scale, a delignified wood veneer was shaped using a mold characterized by varying radii of curvature. When the obtained shape was rewetted, softening of the delignified wood, caused by the decreased interaction between neighboring fibers, allowed for a repeated shaping of the material (Figure 1a,b).

In order to gain a detailed insight into the underlying mechanisms, microscopic investigation by AFM imaging was conducted. In the dry state, the cell walls of the fibers are in close contact to one another, shown schematically in Figure 1c. In the former cell corner regions, shrinkage resulted in a sawtooth-like interlocking pattern between neighboring cell walls (Figure 1d). This tight interlocking combined with frictional forces and hydrogen bonding between OH-groups of the cellulose fibers leads to a stiff and strong material, even in the absence of lignin. The morphology was found to gradually change with increasing water content. First, water absorption in the cell walls results in a swelling and regaining of their initial round shape (intermediate state). In the wet state, free water accumulates between fibers as shown by in situ AFM images (Figure 1d). Softening of the cellulosic scaffold upon water uptake is further shown by the corresponding mechanical properties. Tensile tests performed on 5 mm thick delignified bulk wood samples revealed an elastic modulus of 6.5 GPa (Figure 1e, orange curve) in the dry state. When testing samples at the intermediate state with a water content of 22.9%, an elastic modulus of 3.8 GPa (black curve) was measured. This can be explained by the onset of swelling accompanied by decreased interactions between the cells. In the wet morphing state, water allows for a strong plastic formability with very little stress build up at increasing levels of strain, shown by the tensile
curve in blue. The decrease in strength after reaching a maximum value of 125 Pa corresponds to a slip-off mechanism between fibers, which is crucial for successful shaping of the material.

![Figure 2](image_url)

Figure 2. Bending of a delignified bulk wood sample in the morphing state results in (a) a shear deformed, curved sample. The sample shows vertically aligned edges (red line) after bending. The red dotted line illustrates the orthogonal to the neutral axes that would be expected for perfectly bonded interfaces. b) Densification of a delignified veneer in a cast ceramic mold followed by drying results in a stiff material due to the locked cell corners. c) Wet delignified wood drapes onto the mold while partially delignified wood veneers wrinkle and rupture. d), e) Light-microscope images of delignified and partially delignified veneers after densification in the mold demonstrate that complete removal of lignin is required to disengage mechanical interlocking of cell walls.

The shear deformation mode between de-coupled neighboring fibers is visualized by bending of a delignified bulk wood sample as illustrated in Figure 2a. A bending deformation of perfectly coupled fibers would result in an edge orthogonal to the neutral axes, which was not observed for the delignified wood sample. Instead, vertically aligned edges demonstrate that there is low interfacial shear transfer between the fibers, which allows the wood cells to easily slide past one another. Considering the importance of a sufficient de-coupling of neighboring fibers to allow shear deformation of the material, the role of remaining lignin after delignification has to be investigated. Partially delignified wood molded in the same manner as shown in Figure 2b, was not formable to the curvatures (radii between 200 µm and 7 mm) of the mold, shown in Figure 2c-e. The fibers were observed to wrinkle and rupture upon shaping, being especially apparent in the latewood regions of the sample. This can be explained by the higher lignin content remaining in the latewood after partial delignification compared to earlywood (Figure S1), which strongly
affects the shear modulus of the wood. This rupturing could be observed on both, macroscopic scale and microscopic scale (Figure 2c-e).

Figure 3. a) Stacking results in FVCs between 20% before densification up to values of 85% upon densification. b) Tensile elastic modulus and (c) strength versus normalized FVC demonstrate the broad range of properties that can be achieved. d) Elastic moduli compared to the Voigt model. e) Specific elastic modulus and (f) specific strength for FVCs between 20 and 85%. g) Light-microscope images show the densification behavior of delignified early- and latewood at 20, 60 and 80% FVC. h) AFM images on cell wall level of 20, 60 and 80% FVC samples show notable wrinkling at FVCs above 60%.

The mechanical properties of delignified wood were adjusted by varying the density locally, which directly impacted the stiffness and strength behavior of the material. To measure the stiffness and strength of the material at different densities, tensile tests were conducted on densified cellulose
materials with fiber volume contents (FVCs) between 20% and 85%. Thin delignified bulk wood samples with matching growth ring positions were stacked and densified in radial direction as shown in Figure 3a and the FVC was controlled by the number of used layers and by the resulting thickness after densification. Of note, the achieved values of 85% FVC are far beyond the typical 65% FVC of continuous fiber-reinforced composites and in contrast to the later, no polymeric matrix was needed, as the wood cells were mechanically interlocked.

Depending on the FVC, a stiffness between 5 and 35 GPa (Figure 3b) and corresponding strengths between 60 and 270 MPa (Figure 3c) were obtained. A linear increase in stiffness and strength with increasing fiber volume content has been observed until 60%, which is a typical behavior for continuous fiber-reinforced materials in axial loading, described by the Voigt model (Figure 3d). Despite the delignified wood being a short fiber-reinforced material, the slope corresponds to the Voigt model, assuming an elastic modulus of 40 GPa for single wood fibers[17]. Hence, in the dry state the close contact between the fibers combined with mechanical interlocks and hydrogen bonding allows for excellent stress transfer, resulting in a continuous fiber-reinforced material-like behavior in this matrix free wood composite.

Light-microscopy and AFM imaging were used to analyze the densification process of the stacked samples on a tissue- and fiber level. A densification up to FVC of 60% mainly results in a densification of the earlywood (Figure 3g). At this densification level, the latewood was not yet compressed, but rather started to wrinkle on the cell wall scale, as seen in the AFM images (Figure 3h). At 60% FVC, latewood cells are slightly deformed and show a transition to a completely densified state at 80% FVC. Interestingly, at a FVC of 80%, a higher than expected increase of the elastic modulus is observed. This suggests an improvement of mechanical properties, which cannot solely be attributed to the increased FVC and is supported by the increase of specific elastic modulus with FVC. Possible contributions to these phenomena could include increased hydrogen bonding interactions and additional friction forces, enabled through the close contact between fibers. Additionally, enhanced mechanical interlocking and entanglement between fibers caused by the densification could contribute to increased stiffness. In contrast, at a FVC of 85%, lower values than the predicted Voigt model were obtained for the elastic modulus. This is likely explained by difficulties in the manufacturing process of samples with FVC above 85%, which resulted in deviations in the unidirectional fiber arrangement and potential damage to the cellulose fibers within the samples.
Figure 4. (a) Illustration of fiber alignment and density gradients in a wood ray and in a tree branch attachment to the trunk. The concept of fiber alignment is transferred to the delignified, densified wood for a prescribed load path by a combination of tuned reinforcement, laminate stacking and gradient densification. b) The wood was treated by a TiO$_2$/PDMS coating to obtain delignified-superhydrophobic wood, allowing the material to remain robust against moisture ingress for usage under wet conditions. c) Native, delignified and delignified/densified wood was magnetized to demonstrate the possibility to gain enhanced functionality by using delignified and densified wood compared to native wood. e) Shaped, magnetic, superhydrophobic delignified wood as a proof of concept.
A local variation of the FVC within one sample by topographic stacking leads to mechanical gradients and can be combined with other tree-inspired concepts such as adjusting the fiber alignment to reduce stress concentrations.\cite{18, 19} The demonstration of an open hole structure shown in Figure 4a illustrates the possibility of combining both, fiber alignment and density gradients in one manufacturing process. The fiber alignment of the delignified veneer was pre-programmed by simply shaping the material in wet state. This mimics design principles that are common to native wood structures such as a branch attachment on the macroscopic scale\cite{19, 20} or the adjusted fiber orientation around wood rays on the microscopic scale as shown in Figure S2. Additional delignified veneers could be placed and densified at highly-loaded regions, providing local reinforcement by in-plane density gradients as illustrated in Figure 5a. Figure 5b shows a topographically stacked 0/90° lay-up material with layers increasing from 2 (left side) to 5 (right side), resulting in a density gradient. Alternatively, in plane mechanical gradients were obtained through local densification causing continuous density gradients with reduced thickness in the highly-densified regions (Figure 5c,d).

While formability of the material in its wet state is a major advantage, when being used for load-bearing scenarios, the strong decrease in mechanical performance under wet conditions prevents structural applications. The desired shape could be permanently kept in the interlocked state by superhydrophobizing the surface as shown in Figure 4b, which allows for continued integrity of the structure due to repellence of water. A delignified veneer was dip-coated with a suspension
of TiO$_2$ nanoparticles dispersed in PDMS/THF providing a hydrophobic coating with high abrasive resistance.$^{[21]}$ SEM imaging (Figure S3) revealed a homogeneous coverage of the hydrophobic TiO$_2$ nanoparticles on the surface of the delignified wood. Contact angle measurements were performed in order to investigate the performance of the coating. For uncoated native wood, the static contact angle (115°) decreased with time, as water started to penetrate into the hydrophilic surface. For the delignified samples, the initial contact angle of 50°, is about 50% less than native wood and decreases over time in an even more pronounced manner due to the removal of the hydrophobic lignin. On the PDMS and TiO$_2$ treated surface however, the initial contact angle of approximately 150° remains constant with time (Figure S4).

To demonstrate the possibility of combining mechanical gradients with tunable functionality, magnetite (Fe$_3$O$_4$) and maghemite (γ-Fe$_2$O$_3$) were in situ synthesized inside native and delignified wood by co-precipitation of ferric and ferrous salts (Figure S5, S6). The precipitated particles carry a net magnetization in the presence of an external field. The delignified magnetic wood showed significantly higher values for saturation magnetization (Figure 4c) and susceptibility (Figure S7b) compared to native magnetic wood. Upon densification in the radial direction, the magnetic moment and the susceptibility were further increased. Magnetic moment values of 1.2, 3.6 and 6 emu cm$^{-3}$ were obtained for the native wood, delignified wood and the densified delignified wood, respectively. A similar trend was observed for the susceptibility with a pronounced anisotropic behavior due to the intrinsic microstructure of wood (Figure S7b). SEM imaging revealed the reason for the difference in magnetization between delignified and native functionalized wood. Iron-oxide nanoparticles were mainly in the lumen of the native functionalized wood (Figure S7c,d) and functionalization was not observed at the interface between neighboring fibers (middle lamella), which indicates that the infiltration of the precursor solution mainly takes place via the lumen of the cells. Contrary, the magnetic delignified wood additionally showed nanoparticles in the interface regions between neighboring fibers (Figure S7d). This suggests that the precursor solution was able to not only infiltrate through the lumen, but also via the free space created between neighboring fibers through swelling. Finally, topographic stacking of magnetized delignified wood, followed by a densification in a shaped mold, led to tunable wood comprising bioinspired fiber alignment combined with mechanical and functional gradients (Figure 4d).
Conclusion

In conclusion, wet shaping of delignified wood and the implementation of structural and chemical gradients allows for locally tuning shape and mechanical properties in a predictable manner, which offers the possibility to turn natural wood into a versatile engineering material with excellent mechanical performance. The shaping mechanism is based on moisture triggered reversible interlocking between neighboring cells, which enable shear deformation in the wet state. Upon drying, mechanical interlocks and hydrogen bonding result in a stiff structural material, which can be further enhanced upon densification. Mechanical gradients were created by simply adjusting the density of the material to obtain very high FVCs up to 85%, and elastic moduli of 35 GPa at 270 MPa strength. The concept was further extended by using magnetically functionalized delignified wood, leading to tunable functionality across individual samples by adjusting the density. Additionally, a surface hydrophobization can protect the matrix-free wood from moisture. This approach demonstrates the possibility to create mechanical gradients with tunable functionality in wood and has broad relevance in the emerging field of sustainable high-performance materials.

Experimental Section

Delignification

Norway spruce samples were delignified following the previously established protocol published in Frey et al., 2018. The reaction time was adjusted according to the sample dimensions and is summarized in Table S1. After delignification, all samples were washed with deionized water until the washing solution reached a pH value above 5 and were conditioned at 65% RH / 20°C until a constant mass was obtained.

Preparation of tensile test specimens

Specimens with fiber volume contents (FVC) between 20% and 85% were prepared by densification (see Supplementary methods). Beech tags with an angle of 45 ° were glued to the grip section of thin bulk samples. Prior to mechanical testing the samples were conditioned in 3 different environments: 65%, 95% relative humidity and water saturation.

Shaping of delignified veneers

Delignified wet veneers (t = 0.9 mm and 1.5 mm) were shaped and densified in closed molds with varying radius of curvature followed by vacuum drying. Molds were manufactured in two steps. First, the negative form was 3D printed with an Ultimaker 2+ (Ultmaker, Netherlands) and 1.75
mm thick PLA filaments (BQ, Spain). In a second step, the cast ceramic (Giluform, Suter Kunststoffe AG, Switzerland) was poured into the PLA form to obtain the positive mold.

**Author contributions**

M.F. and T.K. conceived the study. M.F., G.B., M.A-V., M.Z., Y.W, K.T. and A.M.H performed experiments and analyzed data. M.F., K.M., T.K., and I.B. co-wrote the manuscript. All authors discussed the results and commented on the manuscript.

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Publications

References

4.3. Fabrication and Design of Wood-Based High-Performance Composites

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Abstract

Densified delignified wood is a new promising and sustainable material that possesses the potential to replace synthetic materials, such as glass fiber reinforced composites, due to its excellent mechanical properties. Delignified wood, however, is rather fragile in a wet state, which makes handling and shaping challenging. Here we present two fabrication processes, closed-mold densification and vacuum densification, to produce high-performance cellulose composites based on delignified wood, including an assessment of their advantages and limitations. Further, we suggest strategies for how the composites can be re-used or decomposed at the end-of-life cycle. Closed-mold densification has the advantage that no elaborate lab equipment is needed. Simple screw clamps or a press can be used for densification. We recommend this method for small parts with simple geometries and large radii of curvature. Vacuum densification in an open-mold process is suitable for larger objects and complex geometries, including small radii of curvature. Compared to the closed-mold process, the open-mold vacuum approach only needs the manufacture of a single mold cavity.

Introduction

The development of novel natural fiber (NF) based composites equipped with superior mechanical properties represents one of the main tasks in materials science, as they can be sustainable
alternatives for current synthetic systems such as glass fiber composites1-3. Besides traditional NF composites (flax, hemp, kenaf, etc)4,5, the densification of wood after partial or complete removal of matrix components has received increasing attention in recent years6-11. The top-down fabrication route, based on delignification of bulk wood followed by densification, is conceptually contrary to rather complex bottom-up processes for pulp and slurry based products.12 In pulp and slurry based products, the beneficial wood fiber alignment is not retained as fibers are separated in the process. In contrast, structure-retaining delignified wood, which is obtained in a top-down process, transfers the sophisticated architecture with aligned cellulose fibers into the new material. To achieve densification of delignified wood without fiber alignment distortions, new processing routes must be developed.

Direct densification of water-saturated delignified wood samples leads to a limited densification degree, cracks, and fiber alignment distortions due to the wet-sample-inherent free water that creates a counter pressure during densification. Current solutions to avoid structural integrity loss upon densification includes utilization of partially delignified wood followed by high-temperature densification9 or pre-drying of delignified wood prior densification6. Both methods enhance connectivity between neighboring cells, either due to the remaining lignin that acts as glue or free water removal between cells.

In both cases, reduced formability occurs, which limits design applications; the required sample pre-conditioning also leads to longer processing times. Therefore, a fast and scalable process that combines shaping and densification in a single step is necessary.

In this regard, we present here open/closed-mold densification and vacuum processing of delignified wood as methods to combine shaping, densification, and drying in a simple and scalable approach. Figure 1 shows densified delignified wood-composite parts, which were obtained by using the techniques described in this work.
Figure 1: Examples of delignified densified wood composite parts. (A) Door panel, (B) side mirror, (C) door handle of a car, (D) orthosis, (E) cut open helmet, and (F) tachometer cover of a car.

Protocol

1. Delignification of wood veneers

**NOTE:** This delignification protocol is based on our previous works, published by Frey et al. 2018\(^6\) and Segmehl et al. 2018\(^{13}\).

1.1. Mount a stainless-steel sample holder in a crystallizing dish or in a beaker and place a magnetic stir bar below the sample holder. Stack wood veneers on top of the holder and separate them by metal meshes or metal mesh stripes (Figure 2A). Here, we use radial cut spruce veneers with a thickness of 1.5 mm. Wood species and type (tangential, radial, rotary cut veneer) as well as the thickness of veneers can be varied.

1.2. Prepare a 1:1 volume mixture of hydrogen peroxide (30 wt%) and glacial acetic acid and pour the mixture into the crystallizing dish until the veneers are fully covered. Use glass dishes (e.g. Petri dish) to keep the veneers in the solution. Soak samples in the solution at room temperature (RT) overnight while stirring at 150 rpm.

1.3. Heat the solution to 80 °C and run the reaction for 6 h for full delignification. Adjust the delignification time depending on the sample thickness.

1.4. After delignification, pour the delignification solution into an empty beaker and let it cool down before disposal. Gently rinse the delignified veneers multiple times with deionized water. Then, continue washing the veneers without stirring by filling the crystallizing dish (beaker) with...
deionized water. Replace the water twice a day until a pH value of the washing water of above 5 is reached (Figure 2B).

1.5. Handle wet delignified wood veneers with care, as the cellulose scaffold is rather fragile. Use a metal mesh as support for transportation and draping (Figure 4).

![Figure 2: Delignification setup.](image)

**Figure 2: Delignification setup.** (A) Crystallizing dish with metal mesh sample holder and wood veneers stacked on top of the sample holder. Metal mesh stripes separate the individual veneers from each other. (B) Delignied veneers covered by water during the washing process.

2. **Storage and “cellulose prepreg” production**

2.1. Consider processing the wet delignified wood samples within 2–3 weeks. Alternatively, preserve the material for long-term storage in ethanol (EtOH) or dry the sheets between metal meshes.

2.2. Store the dry, flat cellulose sheets (“cellulose prepregs”) below 65% relative humidity (RH). Rewet the sheets in water prior to further shaping and processing.

3. **Densification and forming of delignified wood in closed molds**

3.1. Use closed molds made out of an open-porous material (e.g. ceramic molds, porous 3D printed polymer molds) to enable water removal and sufficient drying. Pore sizes should be below 2 mm, especially towards the surface, to obtain a smooth surface of the final composite part.

3.2. Condition the delignified wood at desired RH. For curvature radii in the cm range or plane structures, use samples that are conditioned at 95% RH at 20 °C. For smaller curvature radii, drape the veneer in water-saturated state, pre-dry the draped material in an open mold at 95% RH, or pre-dry the material in an oven (65 °C) for 5–30 min (the time is depends on the sample thickness). Curvature considerations are made in relation to veneer thickness (here 1.5 mm).

3.3. Densify the material in the closed mold either by using screw clamps or in a press. Readjust the pressure if needed to compensate for shrinkage. The drying process can be speed up by placing the mold into an oven at 65 °C or by increasing the temperature of the press.
NOTE: A relatively low pressure in the range of a few MPa is sufficient to densify wet delignified wood. The final thickness can be controlled by using spacers with the targeted thickness between the mold surfaces rather than by controlling the pressure.

3.4. After full drying, demold the composite part and reuse the mold for a new run.

4. Vacuum shaping and densification of delignified wood in open molds

4.1. Use a porous open mold as described in 3.1. Alternatively, use non-porous molds with a porous layer (e.g. mesh, textile, breather) on top of the mold or on top of the delignified wood to enable drying (Figure 3A).

4.2. Use a textile layer (e.g. peel-ply) to protect the mold from contamination. Drape a water-saturated delignified veneer on top of the textile (Figure 3B) and cover it with a second textile layer and flow mesh.

NOTE: To obtain a smooth surface finish, we recommend using porous closed-mold processing. For this, replace the flow mesh with the porous top part of the mold. However, if surface patterning with e.g. a mesh is desired, the open-mold process is a good alternative.

4.3. Place the mold on top of a stainless-steel plate, apply sealing tape and vacuum tubing, and wrap the mold (open or closed) with a vacuum bag. Use flow mesh to enable water flow to the vacuum tubing. Optionally, place additional mesh layers below the mold to enhance the drying process and to avoid local vacuum pressure drops, especially for bigger parts (Figure 3C).

4.4. Apply a vacuum for drying and simultaneous densification of the composite. For accelerated drying, place the setup into an oven at elevated temperature (e.g. 65 °C).

NOTE: Make sure to use cold traps to avoid water entering the vacuum pump. We here use an oil pump in a pressure range of 10^{-2} bar. However, it is also possible to use a membrane pump but trade-offs regarding densification degree might need to be taken into account.

4.5. After drying, demold the dry composite and reuse the mold and vacuum setup for a new composite part (Figure 3D).
5. Manufacturing of laminated composite parts

5.1. Manufacture thick multi-layer composite parts by lay-up techniques and choose the fiber orientation angle of the layers (e.g. [0°], [0°/90°], [0°/-45°/90°/+45°]) as in traditional composite manufacturing.

**NOTE:** The number of layers can be chosen depending on the targeted thickness of the final part. However, the vacuum time strongly depends on the size and thickness of the part and ranges from 2 h (single layer, 1.5 mm thick) up to 2 days for an 8-ply part.

5.2. Increase bonding between delignified wood layers by applying adhesive between layers during the draping process. Use a water based adhesive (e.g. starch) which allows combined drying and curing of the adhesive.

**NOTE:** We apply 0.04 g/cm² of a 16.5 wt% starch solution between the layers. However, other water-based glues could be used alternatively.

5.3. Demold the composite part and machine finish by hand or with standard wood tooling (Figure 6E,F).

6. Re-use and recycling of composite parts

6.1. Place delignified non-glued wood composites in water until the part regains formability. Then, either reshape the material to obtain a new product (see Frey et al. 2019) or reduce it to small pieces.

6.2. Reuse the small pieces of delignified wood to create new products inspired by standard pulp techniques (e.g. pulp molding) and finally let the material biodegrade after end of life.
Representative results

Delignification and handling of wood veneers.
Complete delignification leads to a mass reduction of around 40% and a volume reduction of around 20% after drying at 65% RH. Besides lignin, a fraction of hemicelluloses gets removed too. Removal of these components results in a fragile cellulose material (see Figure 4). Using metal meshes as supports eases handling and draping.

Figure 4: Handling of delignified wood in wet state. (A) Fragile delignified wood in its wet state. (B) Handling of the material is eased by using a metal mesh for transportation or (C) for draping the material to a mold. (D) Delignified wood draped on top of a porous 3D-printed mold.

Densification and forming of delignified wood in closed molds.
Densification of water-saturated delignified wood (Figure 5A–C) is demanding, as free water in the scaffold creates a counter pressure upon densification and allows the material to flow during processing. This causes fiber deviations and cracks in the final material (Figure 5B,C). One possibility to bypass these limitations is to use moist pre-conditioned (95% RH and 20 °C), delignified wood. In this condition, delignified wood is still reasonably shapeable and its densification does not lead to fiber alignment distortions and defects.

Pre-conditioned material, however, is more rigid compared to the water-saturated state, which makes it difficult to obtain small curvature radii without material damage. For small curvature radii, wet draping followed by conditioning in an already shaped state prior densification can be used. However, conditioning is rather time consuming and therefore not recommended for large-scale applications.
Figure 5: Closed-mold densification of delignified wood in a wet and moist state. (A) Densification of the water-saturated cellulose material leads to (B, C) cracks and fiber misalignment. (D–F) Densification of moist material, conditioned at 95% RH results in a better preservation of fiber alignment and less defects.

Vacuum shaping and densification of a laminated part in an open mold.
Exemplarily for vacuum shaping, we manufactured a helmet in a self-made gypsum mold using an open-mold process (Figure 6A, B). As lay-up, we draped 2 layers of hexagon-flakes for surface texturing followed by 4 layers of delignified wood veneer in a [0°/90°] lay-up (Figure 6C). The flakes provide an attractive surface design, whereas the unidimensional (UD) layers add strength and stiffness to the composite. We applied 16.5 wt% starch as adhesive between layers to prevent delamination.

Vacuum densification (Figure 6D) leads to full drying of the part within 48 h and densification down to a thickness of 3 mm (1/3rd of the initial thickness). After the vacuum processing, the composite part is demolded (Figure 6E) and the edges are trimmed with a cutter (Figure 6F).

The maximum layup thickness that could be densified and fully dried with the open-molding approach was an 8-layer layup (8 x 1.5 mm veneer) with an end thickness of this part of 2.5 mm, which corresponds to a densification down to approximately one quarter of the initial thickness of dry delignified wood, taking into account the layer shrinkage upon delignification and drying.

To obtain such high densification degrees, a low vacuum in the range of 10^{-2} bar is needed.

Delignified wood composites that are densified to around one quarter of their initial thickness typically achieve elastic moduli values around 25 GPa and strength values in the range of 150-180 MPa, as shown in our previous work (Table 1)7.
Table 1: Literature values for tensile elastic modulus and tensile strength of densified delignified wood.
The vacuum processing results in a densification down to $1/4^{th}$ of the initial thickness, which corresponds to a FVC of 66% (marked in blue).

<table>
<thead>
<tr>
<th>FVC</th>
<th>20%</th>
<th>33%</th>
<th>50%</th>
<th>66%</th>
<th>85%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density ($\text{g/cm}^3$)</td>
<td>0.3</td>
<td>0.5</td>
<td>0.72</td>
<td>1</td>
<td>1.3</td>
</tr>
<tr>
<td>Tensile elastic modulus (GPa)</td>
<td>5</td>
<td>10</td>
<td>15</td>
<td>25</td>
<td>35</td>
</tr>
<tr>
<td>Tensile strength (MPa)</td>
<td>60</td>
<td>90</td>
<td>120</td>
<td>180</td>
<td>250</td>
</tr>
</tbody>
</table>

Figure 6: Manufacturing of a helmet by open-mold processing. (A,B) Molding of the original helmet using a gypsum mold. (C) Draping of two outer layers with hexagon flakes followed by draping the inner 4-layers in a [0/90] layup. (D) Densification and drying of the part by vacuum. (E) Demolding of the dry part and (F) finish using a cutter.

Utilizing flow meshes typically results in a mesh-imprint in the sample. This can either be considered as a process-inherent design strategy or can be prevented by placing an additional thicker textile layer between delignified wood and flow mesh.

Alternatively, closed molds combined with vacuum processing as described in protocol step 4.2 can be used. Regular patterning can be obtained by placing small pieces of delignified veneers in a defined order, as shown before for our example with the hexagon patterning on the helmet.

Problems that can arise during vacuum processing include warpages in the composite part, which are caused by incomplete drying and the occurrence of cracks (Figure 7). Cracks mainly result in delignified wood that was stored in EtOH prior composite fabrication. Therefore, after EtOH storage, we recommend to carefully soak delignified wood in water before further processing. Additionally, careful draping followed by slight densification by hand to remove some free water reduces the risk of cracking.
Re-use or decomposition of composite parts.

Our cellulose-starch composite is all bio-based and can disintegrate in water. On the one hand, the hydrophilicity of the material is a disadvantage, as it leads to reduced mechanical performance when in contact with water. A simple method to protect the composite from liquid water comprises hydrophobic coatings, as we have shown in Frey et al. 2019. On the other hand, a hydrophilic behavior of the material can also be beneficial when it comes to end-of-life use and recycling aspects. The sample can simply be disintegrated in water to smaller pieces and the fibrous slurry can further be used for the production of new fiber-based products as shown in Figure 8. Furthermore, the fibrous material is fully biodegradable, as shown in Figure 9.

Figure 7: Possible problems arising in fabrication of complex geometries. (A) Back view and (B) side view of the manufactured helmet. (C,D) Small cracks due to shrinkage of the material during processing.

Figure 8: Re-use of delignified wood fibers. (A–C) Reduction of delignified wood veneers into small pieces by dispersing the material in water. (D–F) Re-use of the fiber slurry for producing the lining of a helmet. (D)
Reveting of a silicon mold with fiber slurry. (E) Final lining of the helmet. (F) Lining made out of disintegrated delignified wood inside of the hard shell of the helmet.

![Figure 9: Degradation of delignified wood fibers.](image)

**A** Petri dish filled with soil. **B** Placing the fiber slurry on top of the soil and **C** filling it with water. **D** Bio-degradation after one day, **E** after eight days, and **F** after 26 days.

**Discussion**

We present versatile fabrication techniques to obtain high-performance delignified wood–based composites and suggest possible re-use and recycling strategies. Closed-mold processing prerequisites pre-conditioning of the material, as it cannot be processed in water-saturated state. Utilizing a closed-mold process, however, could be the method of choice especially if e.g. there is no vacuum setup available or if a nice (smooth) surface finish on both sides is desired. Open-mold vacuum processing of delignified wood allows for combining shaping, densification, and drying of water-saturated samples in a simple and scalable approach. The technique is applicable for the production of complex geometries and offers a scalable alternative for closed-mold processes. We have manufactured composites by stacking delignified wood veneers using starch as adhesive between layers. Densification down to one quarter of the initial thickness resulted in a final thickness of 2.5 mm of the 8-layer thick composite part. For obtaining a smoother surface finish in the vacuum process, the use of a closed porous mold could be an appropriate alternative.

For both processing methods, we recommend the use of an adhesive system in between delignified wood layers in order to decrease the risk of delamination. For the given example, we
choose starch, as it is a well-known bio-based glue for pulp and paper products, such as paper bags, and is water based. Future works will focus on the fabrication of thicker laminates to resolve current limitations in terms of drying and fiber flow deviations.

In general, vacuum processing of delignified wood has the potential for easy and fast production of large-scale densified cellulose fiber composites. After addressing the material's durability issue by applying proper coatings, water-stable adhesive systems or chemical modification, possible industrial applications may include automotive components such as door panels, floors, and dashboards. Our material could replace metals or fiber reinforced composites in order to reduce weight for better fuel efficiency and to improve recyclability.

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Disclosures
The authors have nothing to disclose.
References


4.4. Delignified Wood-Polymer Interpenetrating Composites Exceeding the Rule of Mixtures

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KEYWORDS: Interpenetrating composites, natural fiber composites, high fiber volume content, cellulose scaffold densification, glass fiber alternative

Abstract

Wood is increasingly considered in sustainable structural materials development due to its hierarchical structure, including an oriented reinforcing cellulose phase combined with carbon-capturing and renewability. Top-down manufacturing techniques can provide direct access to this hierarchical cellulose scaffold for use in new functional materials. For high-performance load-bearing wood-based materials, the volume content of the reinforcing phase needs to be increased to much higher fiber volume contents (FVCs). This has been achieved by structure-retaining delignification followed by densification. The obtained matrix-free materials possess high tensile stiffness due to preservation of hierarchical fiber alignment, however demonstrate low mechanical properties in bending and cannot be used in moist conditions due to their propensity for water absorption. In order to address these two challenges, an interpenetrating wood polymer phase composite is developed using a delignified wood scaffold as a continuous reinforcing phase and epoxy resin as the interconnected matrix phase. We utilize the continuous flow channels in delignified wood for vacuum assisted matrix infiltration in a condition of open continuous porosity in the wood scaffold. Prior to matrix curing, the material is densified in order to increase the FVC, decrease porosity and to reduce density variations in the wood scaffold. Due to the compressibility of delignified cellulose fibers, interpenetrating phase composites (IPCs) with very high FVCs of up...
to 80% could be produced, leading to exceptionally high tensile stiffness and strength of up to 70 GPa and 600 MPa. The obtained stiffness values far exceed the upper limit of the rule of mixtures due to an enhanced stress transfer through mechanically interlocked fiber-fiber interfaces combined with the stiffness providing matrix phase that further aids stress transfer between neighboring wood cells via their pits. This new approach paves the way for an efficient production of high-performance sustainable materials that can be used as alternative for glass fiber reinforced composites or natural fiber composites.

Introduction

In view of depleting resources and rising emissions of greenhouse gases, there is a fast-growing need to replace synthetic engineering materials by renewable materials. Wood is a key material for a transition to sustainable societies and economies because it is bio-based and captures CO₂ during growth. Today, wood is readily available in large volumes at low cost and it combines good mechanical performance with a lightweight design due to a structural optimization towards mechanical stiffness, strength and porosity for water transport in the living tree. However, there are still certain limitations for wood-based materials when it comes to high-end structural applications. Limitations mainly occur because of modest mechanical performance arising from the tree’s optimization for both functions, support and flow conductivity, and from low reliability caused by the heterogeneity of the natural material. Functional wood based materials have been manufactured either by deconstructing wood into smaller pieces and assembling the obtained building blocks in a new architecture in a bottom-up approach, or by direct utilization of the reinforcing cellulose scaffolds after wood modification in a top-down approach. Deconstruction of wood followed by re-assembly eliminates inhomogeneities but it can be difficult to achieve targeted performances in a scalable and efficient way. The top-down approach, aiming at modification and utilization of the hierarchical wood structure, has recently gained importance as it enables the fabrication of wood-based materials with excellent mechanical properties and novel functionalities such as transparency, magnetism, insulation or filtering applications. Wood-based cellulose scaffolds are obtained by structure preserving delignification of wood followed by drying in a scalable top-down manufacturing process. After full delignification and drying, neighboring fibers come into close contact to one other, building an interconnected cellulose phase, enabling stress transfer in the scaffold, even without the need of a matrix. The resulting light-weight cellulose scaffolds can further be densified in order to obtain a very stiff and
strong cellulose bulk material.\textsuperscript{9,17} Alternatively, Song et al. 2018 investigated partially delignified wood scaffolds that were densified by hot-pressing to utilize the remaining lignin as matrix and achieved excellent mechanical performance.\textsuperscript{10} However, partial delignification of bulk wood can lead to compositional inhomogeneities and gradients within the scaffold and the cell walls (Figure S1), which can be avoided by complete lignin removal. Both, partial and complete lignin removal, lead to enhanced exposure of the hydrophilic cellulose, which results in an even more pronounced influence of humidity on mechanical properties compared to natural wood.\textsuperscript{17,18} Subsequently, exposure of densified wood material to water leads to relaxation of internal stresses and partial thickness recovery, also referred to as spring-back effect.\textsuperscript{19} Coatings or polymer infiltration can reduce the influence of moisture and can enhance structural integrity.\textsuperscript{17} Yano et al. 2001 obtained moisture-stable, very stiff and very strong wood-based composites by delignification of carefully preselected wood based on stiffness grading followed by phenolic resin (PF resin) infiltration and densification.\textsuperscript{20-21} However, the need of preselection combined with relatively long infiltration times reduces scalability of this approach.

To address some of these challenges, we fabricate an interpenetrating wood polymer phase composite by structure-retaining delignification of spruce wood followed by an efficient vacuum assisted polymer infiltration and densification (Figure 1). Using the inherent transportation path through lumina and pits, infiltration of a continuous matrix phase results in a complex flow behavior that leads to an interpenetrating phase composite. Densification in the infiltrated state before curing, allows the simultaneous reduction of density variations and increasing of the FVC in the wood scaffold resulting in very high stiffness and strength in an efficient approach and without the use of preselection.
Figure 1. Schematic illustrating the fabrication of delignified wood reinforced polymer (DWRP) composites. Natural wood is delignified, resulting in a continuous open porous structure that can be infiltrated with a polymer matrix and densified to a desired fiber volume content (FVC). The combination of mechanical interlocks and bi-continuous phase structure allows for stress transfer in the composite.

Experimental Section

Delignified wood. For obtaining the cellulose scaffolds, Norway spruce (*Picea abies*) samples with the dimensions 100 x 20 x 10 mm\(^3\) and 100 x 20 x 5 mm\(^3\) (longitudinal x tangential x radial) were delignified for 2 x 6 hours following the protocol reported in Frey et al. 2018,\(^9\) and Segmehl et al. 2018\(^{22}\). Wood samples are placed into a beaker on top of a metal-grid sample holder and an equal-volume mixture of hydrogen peroxide solution (35 wt %, Acros Organics) and glacial acetic acid (Fisher Chemicals) is poured into the beaker. After infiltration over night at RT under stirring, the solution was heated, and the wood pieces were delignified for 6 h at 80 °C. The obtained cellulose scaffolds were washed in deionized water until a pH value above 5 was reached and then the samples were conditioned at 65% RH / 20 °C.

Infiltration of matrix. The cellulose scaffolds were dried in an oven at 65 °C overnight. The dry cellulose scaffolds were then infiltrated with the epoxy resin system RIM 235/RIMH 238 (Hexion, USA) by vacuum assisted resin infusion (VARI). The infusion resin system was chosen due to its low viscosity (1000-1300 mPas) combined with a long pot life (>10h). The epoxy resin and hardener were mixed at a weight ratio of 100:34, stirred and then degassed in a vacuum oven for 15 minutes. The VARI setup, illustrated in Figure S2, was built as follows: Three cellulose scaffolds were placed on a steel plate. A net bleeder (Suter Kunststoffe, Switzerland) was placed between
the inlet and the sample and a breather cloth (Suter Kunststoffe, Switzerland) surrounded the cellulose scaffolds for an eased air flow. Spiral tubes surrounded by breather cloth were used at the in- and outlet to allow for degassing. A rather long distance between scaffolds and outlet of 22 cm was chosen in order to generate a slow flow front of the epoxy, reducing porosity during infiltration of the scaffold. The vacuum bag was sealed using tacky tape (Suter Kunststoffe, Switzerland) and the outlet was connected to the vacuum pump (CVC 3000, Vacuumbrand, Germany). Inlet and outlet were regulated with clamps and the infiltration of the cellulose scaffolds was conducted for 90 minutes.

**Densification.** Densification was conducted in a compression resin transfer mold (CRTM)\(^2\) with 3 cavities to densify three infiltrated samples at the same time under an isostatic pressure and to obtain FVCs ranging from 25% up to 80% depending on the mold spacing. Prior to densification, the mold was coated with release agent (Loctite 770-NC Frekote, Henkel, Germany) and the edges were additionally greased with a Motorex lithium grease. A 0.05 mm thick Teflon foil was placed between samples and stamp to ease the release of the samples after densification. Samples were placed into the mold, and additional epoxy was poured into the mold until a total weight of 50 g epoxy per mold was reached in order to have a constant amount of epoxy. The infiltrated scaffolds were densified using a LabEcon (Fontijn, Netherlands) hot press for 5 hours at 60 °C at a pressure of approximately 3 bar. The thickness of the samples after densification was regulated using aluminum spacers between the press and the mold surface.

**Glass fiber reinforced polymer (GFRP) reference samples.** Samples were manufactured by compression resin transfer molding. A unidirectional (UD) glass fiber fabric, 220 g/m\(^2\), (Suter Kunststoffe, Switzerland) was cut to 150 x 90 mm\(^2\) using a digital cutter G3 M2500 (Zünd, Switzerland). 30 g epoxy and 15 or 8 GF layers were used to produce 50% or 25% FVC composites, respectively. The GFRP reference samples were densified under the same conditions as described for DWRP but in a simple CRTM mold with a flat stamp. Densification and curing was conducted as with the DWRP samples. The FVC of the GFRP samples was determined by ignition loss of cured resin in accordance with ASTM D2584.

**Tensile- and 3-point bending testing.** The samples were cut to the dimensions 100 x 20 x 2.5 mm\(^3\) for tensile testing and 100 x 12.7 x 2.5 mm\(^3\) for bending testing using a circular saw (Proxxon, Luxembourg). The clamping area of the tensile samples was reinforced with 2 mm thick GF plates (Suter Kunststoffe, Switzerland). DWRPs with FVCs of approximately 25%, 50% and 70% were tested in tension and bending using eight samples per batch. Before tensile testing, were
conditioned at 65% RH and 20 °C until constant mass was obtained (duration approximately 1-2 weeks). Tensile properties were determined using a universal testing machine (ZwickRoell, Germany) equipped with a 100 kN load cell at 20 °C and 65% RH in accordance to ISO 527 with an initial clamp distance of 46 mm and a crosshead speed of 5 mm/min. The change in length was measured with a contact extensometer (ZwickRoell, Germany) with an initial length of 20 mm. Three-point bending measurements were used to determine the bending properties of the DWRPs using the universal testing machine equipped with a 1 kN load cell with a crosshead speed of 4 mm/min. In accordance with ASTM D790, the span between the loading supports was set to 80 mm, which results in a span-to-thickness ratio of approximately 32, and the radii of the loading nose and loading supports were chosen to be 5 mm and 2 mm, respectively.

**Microscopy.** Light microscope imaging (Olympus BX51, Japan), scanning electron microscopy (SEM) imaging (Hitachi SU5000, Japan) and atomic force microscopy (AFM) imaging (NanoWizard 4, JPK Instruments AG, Germany) were conducted in order to investigate the infiltration and densification behavior. Cross section cuts as well as longitudinal cuts (radial) were analyzed by light microscopy and SEM. DWRPs were embedded in epoxy potting resin (EpoFix, Struers GmbH, Germany) and the embedded samples were polished after curing using a LaboPol-25 (Struers GmbH, Germany). High quality surfaces for AFM imaging were obtained using an ultramicrotome (Ultracut, Reichert-Jung, Germany) with a diamond trim knife (Diatome, Switzerland). AFM imaging was conducted in the quantitative imaging mode at 20 °C and 65 % relative humidity using a non-contact cantilever (NCHR, Nano World). A set point of 60 nN, z-length of 150 nm and a pixel time of 12 ms was used. The JPK image processing software (JPK Instruments AG) was used to process the images.
Results and discussion

Figure 2. Light-microscopy and SEM images show the complex infiltration behavior in the wood scaffold. (a) Schematic of a delignified wood cube during infiltration along the main longitudinal x-axis. (b) Illustration and light-microscope image of a partially infiltrated radial cut show multiple staircase-like infiltrations taking place and zoom into region of interest to illustrate the infiltration mechanism. Border pits in tangential walls enable a radial flow (y), whereas the bordered pits in the radial wall allow the flow in tangential direction (z) from one cell to the other. (c) Illustration and light-microscope image of a radial cut of a fully infiltrated sample. (d) Cross section of a partially infiltrated sample shows infiltrated latwood cells (small lumen, thick cell walls) and partial infiltration of earlywood cells (large lumen, thin cell walls). (e) Cross section of a fully infiltrated sample and zoom showing structural details proving the infiltration mechanism through lumina and bordered pits: SEM image of a cell corner showing the collapsed middle lamella region, which is not filled with epoxy and SEM image of an infiltrated bordered pit.

Delignification of bulk wood represents a simple top-down approach to manufacture lightweight cellulose scaffolds that are composed of aligned fibers (tracheids). Lignin removal takes place in
between neighboring cells, which leads to an almost complete removal of lignin in the middle lamella and in cell walls, resulting in a higher porosity in wet state. Upon drying, the delignified wood cell walls shrink and neighboring cells get in close contact to each other, leading to cell deformation. This deformation generates wrinkled interfaces, which can act as mechanical interlocks between the cells. These interlocks provide remarkable structural integrity and are responsible for the high mechanical stability even for dry cellulose scaffolds without any resin matrix. Additionally, during structure preserving delignification the cavities in wood cells called lumina are retained. Presumably, interconnections between lumina of neighboring cells are even improved by the partial degradation of bordered pits. This percolating path can be exploited for matrix infiltration into the cellulose scaffold by vacuum assisted resin infiltration (VARI), and allows the infiltration of a hydrophobic matrix into the hydrophilic cellulose scaffold by use of Darcy driven flow combined with capillary pressure of the small flow channels.

To investigate in detail the hydrophobic matrix infiltration through the interconnected path of the pores, radial cuts and cross sections of partially infiltrated and fully infiltrated samples were analyzed by light microscopy. The infiltration behavior observed for the radial cut (Figure 2b) appears to be due to simultaneous infiltration in longitudinal, radial and tangential directions. Part of the matrix filling the lumen in longitudinal direction flows through pits in the tangential walls, which causes a cascaded flow to neighboring cells in the radial direction. At the same time, radial wall pits allow the matrix to spread into neighboring cells in the tangential direction, which results in multiple staircase-like flow fronts. This staircase-like infiltration pattern was found in all regions of the wood, irrespective of the size of the cell lumina; small lumina of cells grown towards the end of the season (latewood tracheids), large lumina of cells grown in the early part of the season (earlywood tracheids) and cells with medium lumen size (transition wood tracheids), which form the majority of the microstructure in spruce.

Observing partially infiltrated sample cross sections to better understand the flow behavior (Figure 2d), suggests that the infiltration in latewood is faster than in earlywood. This can be explained by the smaller cross-sections of latewood lumina compared to earlywood. The capillary pressure is indirectly proportional to the capillary diameter, which results in a higher capillary pressure to promote filling of latewood. However, the epoxy flow also depends on the applied vacuum, which leads to a mixture of capillary flow and pressure driven Darcy flow.

The infiltration finally leads to an infiltrated three-dimensionally interconnected matrix phase (Figure 2c,e). Only some minor voids and small air bubbles were visible as a result of the
heterogeneity in permeability of the scaffold and the resulting race-tracks flow. Zooming into the infiltrated cross section by SEM (Figure S4) reveals that infiltration only took place in cell lumina and pits and that the interface between cells and the cell corner regions were not penetrated by the matrix. Therefore, the interaction between neighboring fibers is a combination of close contact between cell walls and their mechanical interlocking in the former middle lamella and cell corner regions as previously observed for non-infiltrated scaffolds\textsuperscript{17} and the through pits interconnected polymer phase.

**Figure 3.** (a) Schematic of the densification of infiltrated samples to different FVCs. (b) Densification curves of cellulose scaffolds conditioned at 65% RH with high (0.38 g cm\textsuperscript{-3}) and low (0.27 g cm\textsuperscript{-3}) densities. (c) Light-microscope images of DWRP with FVCs ranging from 18% (no densification) up to 70% FVC. The thin walled earlywood cells start folding at low densification forces (1-2 MPa), whereas transition wood and the thick walled latewood require higher densification forces.
The ratio of reinforcing cellulose phase to matrix phase is increased upon densification. Figure 3a illustrates the densification of matrix infiltrated delignified wood prior matrix curing. We adjusted the FVC by varying the final thickness of the composite to achieve values of FVC between 18 % without densification, and up to 70-80 % for highly densified samples, depending on the initial density of the sample. The high pressures during isostatic pressing in the CRTM mold allowed the elimination of air bubbles in the epoxy and full infiltration of the scaffold.

To investigate cell folding patterns during densification, we densified non-infiltrated delignified wood scaffolds of different densities in steps and analyzed the corresponding stress-strain curves (Figure 3b,S3). Density differences of delignified wood correspond to different earlywood, transition wood and latewood ratios within the wood sample and influence the densification. First, there is a plateau at low densification forces (1-2 MPa), corresponding to the densification of thin walled earlywood cells. Then, the force constantly increases upon densification of transition wood (> 5 MPa) and finally latewood (> 10 MPa). This is due to lower thickness of earlywood cell walls compared to latewood cell walls, and their larger cell diameter. It follows that a high density scaffold typically contains a lower earlywood content and requires higher densification forces at lower strain than a scaffold with a low density as shown by the densification curves of a high-density (0.38 gcm$^{-3}$) and a low density (0.27 gcm$^{-3}$) delignified wood scaffold (Figures 3b, S3). Sharp transitions in the densification force between earlywood, transition wood and latewood are not observed due to a gradual change in density and due to mixed-mode buckling behavior depending on the thickness of the cell wall and on the loading condition. Pure Euler buckling would estimate up to six times higher force needed to buckle the latewood cells for the same buckling mode or 1.66 times higher force for a higher earlywood buckling mode (see SI Methods).

Polished cross sections of DWRP at varying FVCs (Figure 3c) show a folding pattern that is similar to non-infiltrated delignified wood samples that were previously observed. With our new approach, it is possible to manufacture DWRPs with FVCs up to 70-80%. This is beyond the practical maximum fiber content of fiber reinforced composites, which is theoretically 70% and practically around 63-65% usually even lower for plant fiber reinforced composites due to their irregular shape. In contrast to traditional plant fiber composites (e.g. flax, sisal), the polymer matrix in DWRPs fills the luminal cavities and the pits, while the outer fiber surface is in close contact to the outer surface of the neighboring fiber.

Processing of very high FVC samples above 80% is still challenging, as the cellulose scaffold starts to deform in shear. This can lead to deviations in fiber alignment from the unidirectional fiber
arrangement of the scaffold. Some process related cracking of the sample can be observed at lower FVCs as shown in Figure 3 and the light microscope image of a polished surface of a 50% FVC DWRP (Figure S4a) reveals some cracks that may have been caused by polishing or by shrinkage of the matrix during curing. It is interesting to note that cracks are mainly present at the fiber-fiber interface of neighboring cells, resulting in fiber bridging, or in the cell walls as shown in Figure S4b. This suggests a good interfacial adhesion between the epoxy and the cell wall. Zooming into a fiber-matrix interface by SEM (Figure S4c) further shows a wrinkled interface (dashed line) caused by the densification and wrinkling of the cell wall. AFM imaging (Figure S4d) reveals an additional wrinkling at the nanometer scale.

Figure 4. Tensile properties of DWRPs compared to native wood, delignified wood (DW) and glass fiber reinforced polymer (GFRP) composites. (a) Tensile modulus and (b) tensile strength of the composites as a function of their relative FVC. (c) Rule of mixture (ROM) and Halpin-Tsai models compared to the experimental tensile moduli of DWRP demonstrate that their modulus exceeds the bounds of theoretical predictions. (d) Specific tensile modulus versus specific tensile strength for comparing the density normalized properties of the studied composites.

To investigate the influence of the FVCs on the mechanical properties of DWRPs, tensile and bending tests were conducted on samples with FVCs around 25%, 50% and 70%. The results were compared to reference materials including native wood, delignified wood (DW) and glass fiber
reinforced polymer (GFRP) composites. High FVCs of 70% and above were only achieved for DWRPs due to the ability of delignified wood to be densified. For non-infiltrated DW, a FVC of 70% and above was not obtained due to the spring-back effect, which was observed after densification of oven-dried cellulose scaffolds. The achievable volume fraction of the GFRP was limited due to incompressibility of glass fibers and the type of fabric used. While traditionally, contact of neighboring fibers is not desired, in DWRPs, the contact is advantageous because it enhances the interface due to mechanical interlocking of the deformed cells. The deformability enables a closely packed composite with FVCs of above 70%, resulting in materials with remarkably high tensile stiffness of up to 70 GPa and tensile strength of about 600 MPa.

While tensile stiffness (Figure 4a) and tensile strength (Figure 4b) both increase with rising FVC, the increase in stiffness far exceeds predictions from traditional fiber reinforced composite models, such as the Halpin-Tsai model (see SI), which predicts the elasticity of a composite material using the elastic properties of matrix and filler as well as the orientation and geometry of the reinforcing phase. The reported values even exceed the upper limit rule of mixture (ROM, see SI) as seen in Figure 4c, assuming an elastic modulus of a single delignified wood fiber of 50 GPa and an aspect ratio of 100. A similar trend was found to be true for matrix free composites, implying that fiber-fiber interactions at high FVCs govern stress transfer ability and allow attainment of mechanical performance exceeding traditional theories.

For observing this effect, high FVCs are needed, which requires a deformable interconnected phase with aligned reinforcing elements. Therefore, delignified wood provides an excellent reinforcing scaffold for high-performance interpenetrating phase composites. Additionally, the low density of cellulose fibers results in high specific tensile properties and DWRPs with high FVC even outperform all tested reference materials regarding specific tensile properties as shown in Figure 4d and are among the best performing composites compared to previously reported natural-fiber reinforced composites (Figure S5). Tensile elastic moduli and strength as well as densities of DWRPs and reference samples are reported in Table S1. To further study the mechanical behavior of the DWRP composites in a more complex loading environment, bending measurements were conducted.
Figure 5. Bending properties of DWRP in comparison to the references native wood, delignified wood (DW) and glass fiber reinforced polymer (GFRP) composites. (a) Bending modulus and (b) bending strength of the composites as a function of their relative FVC. (c) Specific bending modulus versus specific bending strength for the studied composites.

In bending, the influence of the matrix is even more pronounced and DWRPs show much higher bending stiffness and strength compared to the non-infiltrated DW (Figure 5a,b), which demonstrates the importance of the interconnected penetrating polymer phase specifically for this loading condition. The DWRP was found to have a similar bending stiffness as GFRP, although the bending strength of GFRP is approximately twice the bending strength of DWRP. This can be explained by analyzing typical stress-strain curves and fractures of 50% FVC samples (Figure S6). The GFRPs show a brittle tensile-dominated failure at 800-900 MPa, whereas DWRPs exhibit
strong plastic deformation starting in the range of 100-200 MPa prior to a final fracture around 300 MPa. The DWRP fails in a mixture of compression- and tensile-failure as shown in the light-microscopy images in Figure S6. Non-infiltrated DW samples failed in compression and showed a plateau at around 100 MPa. Therefore, the interpenetrating matrix stiffens the DW scaffold by filling the empty space in the lumina and helps to resist compression failure at low stress levels. Additionally, interconnections created by infiltrated pits possibly lead to a higher shear modulus and strength that further enhances the structural integrity of the composite material. Due to its lower density, DWRPs outperform GFRPs in terms of specific bending stiffness, however, GFRPs still have a higher specific bending strength compared to the DWRPs. Bending moduli and strength as well as densities of DWRPs and reference samples are reported in Table S2.

**Conclusion**

We have produced fiber composites showing exceptionally high specific stiffness and strength by the infiltration of epoxy into a wood derived cellulose scaffold by VARI infiltration followed by densification, achieving FVC of up to 80%. Infiltration in longitudinal direction is possible due to a percolating porous network inherently present in the preserved delignified wood structure, which exists even after simple air drying of the cellulose scaffold and eliminates the need for elaborate drying techniques such as freeze-drying. The matrix phase creates an interconnected phase, which surrounds the cellulose scaffold that by itself is interconnected forming an interpenetrated composite. The resulting composite possesses very high tensile stiffness and strength of up to 70 GPa and 600 MPa due to a combination of mechanical interlocks between cells, the reinforcing matrix phase connecting fibers through lumen and pits and a very high FVC of up to 80%. In contrast to synthetic composites, an intimate fiber-fiber contact that allows for very high volume fractions of the reinforcing phase is obtained. This tight contact increases the stress transfer in the composite and leads to an increase in stiffness with FVC, which far exceeds the upper limit rule of mixture (ROM). The reported natural fiber composite is in the range of the highest obtained values of wood-based composites using a technique that is fast, efficient and scalable.

**Supporting Information**

Image of native wood and partially delignified wood; VARI infiltration setup; densification curves of dry, non-infiltrated cellulose scaffolds at varying wood densities; structural characteristics of DWRPs; comparison of specific tensile properties to literature values; representative tensile
stress-strain-curves of GFRP, DW, DWRP and wood; light microscope-images of the fracture after bending of GFRP and DWRP; tables with tensile- and bending stiffness and strength of all tested materials and of reference material; Euler’s critical load for buckling for earlywood and latewood densification.

**Author Contributions**

MF: Designed the study, performed experiments, analyzed data and co-wrote the manuscript; LS: Performed experiments and analyzed data; KM: Designed experiments, Analyzed data and co-wrote the manuscript; TK: Analyzed data and co-wrote the manuscript; IB: Analyzed data and co-wrote the manuscript.

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References


4.5. **Summary of the co-authored publication – Mesoporosity of Delignified Wood Investigated by Water Vapor Sorption**

In this publication, we investigate the influence of partial and complete delignification on the mesoporous structure of spruce wood by water vapor sorption. The mesoporosity of the bio-based scaffold was investigated in different humidity conditions, such as in the fully water-saturated state and in various intermediate states, and porosity analysis was complemented by measurements of hydroxyl accessibility.

The porosity of wood cell walls increases with increasing delignification time and results in a reduced porosity upon full delignification due to pore-collapse upon air-drying. In fully water-saturated state however, the porosity of fully delignified samples is retained. These findings are highly valuable for further development of wood cell wall modification or functionalization.

**Contribution to the publication:** Shared first-author publication. Preparation of samples, conducting measurements and co-writing of the publication.
5 General Discussion and Conclusion

The main goal of this thesis was to develop high-performance natural fiber reinforced materials based on wood-derived cellulose scaffolds. These hierarchical, porous and lightweight scaffolds are obtained by structure-retaining delignification of wood and can further be functionalized, shaped and/or densified. Scaffolds are produced in relatively simple top-down approaches, which open up the way towards new, scalable, wood-based high-performance materials. We presented manufacturing of matrix-free and matrix-infiltrated cellulose materials including detailed analysis of microstructural characteristics and mechanical performance. A specific focus was laid on investigating the interfaces between neighboring fibers, which are important for a good stress-transfer and thus are mainly responsible for the high mechanical properties. Additionally, these interfaces enable the material to be shapeable and tunable. In this chapter, the development of cellulose scaffolds and matrix-infiltrated cellulose reinforced composites is reflected and critically discussed. Further, conclusions regarding scalability and future research in the field of wood-based high-performance materials based on delignified wood are drawn.

Wood-derived cellulose scaffolds are obtained by structure-retaining delignification, which results in the removal of the matrix components lignin and hemicelluloses. This process makes the wood inherent reinforcing cellulose scaffold available, which can further act as new material platform. The scaffold consists of unidirectionally aligned cellulose fibers. Its microstructure, density and mechanical properties, strongly depend on the moisture content (Figure 5). Scaffolds are rather fragile when in water-saturated state. The fragility is caused by water, which enters the porous space in cell walls and between neighboring fibers and minimizes fiber-fiber interactions. This separation of neighboring fibers, as illustrated in Figure 5a, is possible due to the lack of a supporting matrix in between fibers. In consequence, in wet state, the cellulose scaffold is easily shapeable, which is in stark contrast to native wood where lignin and pectin constitute the stabilizing middle lamella.

Figure 5: Influence of humidity on the microstructure of cellulose scaffolds. (a) Scheme of delignified wood in wet state and (b) delignified wood in dry state.
5.1. **Formability of cellulose scaffolds**

Wood or partially delignified wood materials are only shapeable if the lignin matrix is softened. This is usually achieved through water saturation followed by heating.\textsuperscript{110} In contrast, completely delignified cellulose scaffolds can be easily shaped in water-saturated state without applying heat. In the wet, so-called morphing state, water enters the region between neighboring fibers, which allows for shaping of the cellulose scaffold and offers the possibility to create complex shapes with low radii of curvature. The formability is of great importance when it comes to designing shaped delignified wood products. Fibers are able to follow the shape of the part without being cut, which minimizes stress-concentrations.\textsuperscript{111,112} This fiber alignment is crucial for high-performance anisotropic materials and is similarly performed in the production of fiber-reinforced composite parts, where fibers are draped into a mold before infiltration and curing\textsuperscript{113} to ensure the optimal fiber alignment.

The formability of cellulose scaffolds can additionally be utilized to limit stress concentrations by adapting the fiber alignment within layers. This is important for example to optimize structures that contain holes and is inspired by trees that adjust their fiber alignment around branch holes or wood rays.\textsuperscript{73,114} Mattheck et al. reported that the optimized fiber flow around a tree branch hole is achieved when the reinforcing fibers follow the principle stress trajectories, because they are not subject to shear stresses in this configuration.\textsuperscript{72} In the second research article of the thesis we made use of such in-plane tailored fiber alignments to limit stress concentrations around a hole (Figure 5.1). Such an adjustment of fiber flow in the wet cellulose material allowed us to incorporate this tree-inspired fiber alignment concepts at the location of choice by simply adjusting the fiber alignment in wet state.

5.2. **Interlocked interfaces**

In dry state, cellulose fibers get in close contact to each other and form tight fiber-fiber interfaces that equip the scaffold with rigidity. These so-called interlocked fiber-fiber interfaces are obtained due to the removal of the wood inherent matrix lignin in combination with fibers approaching...
close contact to each other upon shrinkage. Interlocked cell corners and suture fiber-fiber interfaces as shown in AFM images in **Figure 5.2a** provide the cellulose scaffold with integrity and mechanical strength as they enable stress-transfer throughout the scaffold.

The concept of interlocking and suture interface design is found in many biological materials, such as in the tissues of walnut shells\(^47\) or the carapace of the red-slider turtle,\(^44,45\) as described in chapter 3.1.3. In the walnut shell, polylobate sclereid cells interlock into a 3D puzzle with neighboring cells by forming concave and convex parts as shown in Figure 5.2b. This tight 3D interlocking provides the tissue with a high ultimate tensile strength.\(^47\) **Figure 5.2c** shows the suture interface between adjacent ribs of the turtle shell and the interlocking between interdigitating fingers in cross-section. The thin soft-tissue interface between the ribs provides the shell with flexibility at low rate deformations but makes it rigid at high-rate loads.\(^44\)

**Figure 5.2**: (a) AFM images of delignified wood cell corners, which show interlocked and suture features at the fiber-fiber interface. (b) SEM images of interlocked polylobate sclereid cells in the walnut shell. Adapted from Antreich et al.\(^47\) (c) SEM images of suture interfaces between two adjacent ribs of a turtle shell, which are interlocked in cross section. Adapted from Krauss et al.\(^45\)

It is well known that the a higher interfacial area can amplify mechanical properties\(^115\) and therefore one could consider in the future to enhance interlocking in delignified wood-based materials by introducing stronger waviness at the interface or by increasing fiber surface
roughness. Other methods to improve the stress-transfer at the interface may include a fibrillation of the fiber surface, which could lead to a mechanical anchoring at the interface as shown by Karlsson et al. for regenerated cellulose fibers. We thus have presented a densification process combining compression and lateral shear in our first article. This method initially aimed for a fibrillation between neighboring fibers and enhanced mechanical interlocking at the fiber-fiber interface. The shear densification resulted in a more homogeneous folding of earlywood and a smoothening effect at the cell-wall level compared to densification without applying shear. However, the shear force was not sufficient to induce the desired fibrillation at the interface. Potential influences of such nanofibrillar effects in delignified wood-based materials have until now only been postulated, but are still under discussion. In order to prove these effects and to obtain fibrillation in the future, our densification setup needs to be optimized. Further possible fiber-fiber interface-modification strategies, which one might consider, are presented in the outlook.

5.3. Tunability and effect of density

An important part of this thesis is the tuning of mechanical and functional properties of delignified wood. The native wood structure is preliminary optimized for mechanical support and transport functions, two mechanisms that are balanced in the wood architecture by cells and matrix that provide structural support and the open path consisting of lumina and pits that enables transportation. Wood-derived cellulose scaffolds can be optimized regarding mechanical performance, mainly by increasing density, or regarding functionalizability. Enhanced functionalizability often goes along with reducing density and making the open porous path more accessible. Therefore, the two optimization techniques are often mutually exclusive. However, a functionalizable material that shows high porosity can be densified after functionalization, which can result in high-performance functional wood-based materials and was explored in the second article.

5.3.1. Functionalizability

A straightforward strategy for improving functionalizability is the increase of porosity, which can be obtained by complete or partial removal of matrix components. In recent years, researchers have used delignified wood for versatile functionalization approaches. Transparent magnetic wood was manufactured by Gan et al. with a simultaneous infiltration of magnetic nanoparticles and MMA followed by polymerization. Others functionalized cell walls of delignified wood
scaffolds and utilized the inherent liquid transportation system for filtration approaches. Fu et al., for example, developed hydrophobic wood/epoxy composites for oil water separation by epoxy infiltration into cell walls of delignified balsa wood. Guan et al. utilized the flexibility of delignified wood scaffolds and presented compressible, oil-absorbing sponges obtained by freeze-drying of delignified wood followed by polysiloxane coating to render the scaffold hydrophobic. The absorbed oil was removed by simple squeezing and the sponges possessed excellent reusability. The inherent transport pathway was also exploited for ionic conductors and flexible electrodes. Delignified wood-based electrodes comprise a multiphase transport system that allows for electrical conductivity, Li⁺ ion transport and O₂ gas transport. They were obtained by Chen et al. by delignifying balsa wood to increase flexibility followed by a carbon nanotube (CNT) and ruthenium nanoparticle coating to incorporate electrical conductivity. Ion- and gas transport was enabled through porous cell walls and lumina, respectively.

Delignification increases the porous space in the wood-based scaffold and therefore enables the incorporation of a higher material load, which eases functionalization. However, porosity strongly depends on the humidity of the scaffold and generally decreases upon drying. In the co-authored article «Mesoporosity of delignified wood investigated by water vapor sorption» we have investigated the moisture dependent porosity of delignified and partially delignified wood. We have observed that the preservation of a partial lignin content in the scaffold reduces the pore collapse upon drying and could therefore be an option, if cell-wall porosity after air drying is required. Cell wall functionalizability can also be enhanced by using elaborate drying techniques such as freeze drying or solvent exchange drying, which both prevent the collapse of cell-wall pores during drying. These techniques have already been used for the manufacturing of transparent wood but are limited in scalability.

In the second article of this thesis, an enhanced functionalization of completely delignified cellulose scaffolds was obtained due to functionalization in water-saturated state because the porosity is maximized in this state. As proof of concept, magnetic nano-particles have been \textit{in-situ} formed within wood and delignified wood scaffolds. Merk et al. reported this \textit{in-situ} co-precipitation of ferric and ferrous salts in native wood and observed a clear directional dependence of the magnetic behaviour that was correlated to the wood structure. Segmehl et al. further introduced a different magnetization technique in order to avoid material deposition in the lumina and demonstrated, that the anisotropic properties result from the wood structure.
We observed such an anisotropic behaviour also for delignified wood. However, the functionality was enhanced after delignification by a factor of approximately three compared to native wood and can be explained by the increased porous space of cellulose scaffolds in wet state, which leads to the deposition of more functional material per volume. Functionality was even enhanced in a second step by densification of the functionalized material, which simply increased the amount of functional material per volume.

Figure 5.3-1a shows a scheme of delignified wood in wet state. The scheme shows that functional material can enter the porous cell walls, lumina, as well as the space between neighboring cells, the former middle lamella. In contrast to native wood, more functional material can enter the scaffold potentially due to the higher porosity at the cell-wall level, but also in the newly created space between neighboring cells. The separation of neighboring fibers by a water layer provides an additional path for the functionalization of the former middle lamella region. In fully swollen state, this path is interconnected, which creates the possibility to deposit a connected phase of functional material with a 3D-network pattern at the tissue level. Such an approach could lead to very attractive functional materials revealing for example electrical conductivity at low weight without filling the lumen path, which can not yet be obtained in a simple approach for native wood.

**Figure 5.3-1:** (a) Scheme of delignified wood in wet state and location of functionalization in red after water-based functionalization. The functional materials penetrate lumina, cell walls and the former middle lamella region. (b) Delignified wood in dry state and location of functional material after infiltration in dry state. The functional material enters lumina and pits only.
wood as the continuous path between fibers is blocked by the lignin/pectin matrix of the middle lamella.

The interconnected path in the former middle lamella can only be exploited in fully water-saturated state. Upon drying, the gap between neighboring fibers closes and the characteristic interlocks are created. Drying additionally results in a collapse of the porous structure on cell-wall level\(^99\) and decreases functionalizability on both, tissue and cell-wall level. However, the open porous path consisting of lumina and pits is still available for functionalization or modification as illustrated in Figure 5.3-1b. In contrast to native wood, this path is better accessible after delignification, because formerly closed pits open upon delignification. This path was utilized for infiltration of a polymer resin followed by densification to improve mechanical properties in the fourth article of this thesis.

**5.3.2. Mechanical properties**

A straightforward strategy to improve mechanical properties of delignified wood is densification, which results in a decrease of pore volume and simultaneously an increase of the load-bearing cellulose volume fraction. However, fiber damage upon densification needs to be prevented. If the material is only partially delignified, hot densification, which is similarly used for wood densification,\(^{122}\) needs to be applied as presented by Song et al.\(^93\) Partial delignification followed by hot densification resulted in a very high tensile strength of up to 580 MPa and a stiffness of approximately 50 GPa without the addition of a polymer matrix system.\(^93\) Even without any lignin matrix, densified cellulose scaffolds possess remarkable tensile properties of up to 40 GPa in stiffness and a strength of up to 300 MPa. In contrast to the approach of Song et al., densification of completely delignified wood, is conducted without applying heat and scaffolds are shapeable before densification.

We combined the formability aspect of delignified wood with the possibility to create thickness or density alterations inspired by the structure of a tree branch hole as shown in Figure 5.3-2. A tree, not only optimizes fiber alignment, but also locally adjusts material properties. Delignified wood-based materials

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**Figure 5.3-2:** Adaptive growth around a tree knot hole\(^74\) and transfer to delignified wood materials in Frey et al. 2019.\(^15\)
properties can easily be varied by local stacking of layers to increase thickness followed by an optional densification that results in a homogeneous thickness and density alterations.

In general, with increasing density, tensile stiffness and tensile strength of delignified wood-based materials increase when cellulose fibers are not damaged during densification. We reported in the second publication an increase in mechanical properties up to a critical fiber volume content of approximately 80%. Above 80%, a drop in stiffness was obtained potentially due to defects such as fiber deviations that occurred during densification with very high-forces. Fiber deviations from the ideal unidirectional alignment are more prone to occur in higher humidity samples as interlocking between neighboring fibers is less pronounced at this condition. This weakening of fiber-fiber interfaces facilitates shear movement between fibers during densification. Therefore, the choice of appropriate scaffold humidity for the applied densification technique is crucial and was highlighted in the third article.
5.4. **Matrix infiltrated cellulose scaffolds**

In the fourth article, we presented the infiltration of a hydrophobic matrix into the cellulose scaffold. The open porous path of dry delignified wood was filled with an epoxy resin by vacuum assisted resin infusion (VARI). The infiltration through lumina and pits was followed by densification of the scaffold and curing of the matrix, which resulted in very stiff and strong interpenetrating cellulose-polymer composites. Matrix-infiltrated scaffolds reveal improved tensile and bending properties compared to their matrix-free counterpart and tensile values reached up to 70 GPa in stiffness and 600 MPa in strength. This is in accordance with densified preselected cellulose-PF composites manufactured by Yano et al.\textsuperscript{10}

The vacuum assisted infiltration of the polymer into cellulose scaffold is adapted from well-established infiltration processes in the composite industry.\textsuperscript{123} Nevertheless, the resulting microstructure and properties of the cellulose scaffold reinforced polymer differ from traditional unidirectional fiber reinforced composites.

Traditional unidirectional fiber reinforced composites for structural applications mainly comprise the use of continuous synthetic fibers such as glass fibers and carbon fibers or natural fibers. Synthetic fiber reinforced plastics possess high mechanical properties and especially the tensile properties of carbon fibers are out of reach for natural fibers.\textsuperscript{124} However, natural fibers such as flax, hemp or sisal are increasingly considered for replacing glass fibers in structural components, for example in the automotive industry,\textsuperscript{125,126} due to the lower environmental impact combined with sufficient mechanical properties.\textsuperscript{23,127} Research towards structural composites based on natural fibers focused on non-wood fibers.\textsuperscript{22,27,76,128-130} In this thesis, we presented wood fiber-based structural components, with the aim to achieve comparable or even better mechanical properties compared to non-wood fibers and their synthetic alternatives.

Traditional continuous fiber reinforced polymers (FRPs) consist of stiff fibers that are embedded in a matrix. The matrix, acts as glue between neighboring fibers, and transfers stresses from one fiber to the next. Main factors that influence the mechanical properties of continuous FRPs comprise the type of fiber, matrix and interface and the fiber volume content. Figure 5.4a illustrates the microstructure of a traditional continuous FRP and highlights the fiber-matrix interface that is crucial for stress-transfer in the composite part.\textsuperscript{5,31} The separation of neighboring fibers by the matrix is important as it minimizes the risk of fiber damage.\textsuperscript{31,131}
The traditional architecture of such unidirectional fiber reinforced composites is in stark contrast to the microstructure of delignified wood-based composites. Unlike traditional fiber reinforced composites that rely on a matrix for stress transfer, delignified wood-reinforced polymers comprise an interconnected cellulose scaffold that inherently possesses high mechanical properties without an additional matrix, caused by the interconnected fiber-fiber interfaces (Figure 5.2.1b). The embedding of a matrix into the delignified wood scaffold, as illustrated in Figure 5.2.1c, leads to improved mechanical properties and was reported in the fourth article of this thesis. Delignified wood reinforced composites can obtain very high fiber volume contents that exceed the maximum FVC of continuous FRPs, enabled by the deformability of the cellulose scaffold and the cell walls.

**Figure 5.4:** Scheme of the microstructure of (a) traditional fiber reinforced polymers with fibers (grey) embedded in a matrix (blue) connected by the interface (orange), (b) delignified densified wood consisting of cellulose fibers (grey) and fiber-fiber interfaces (orange). The interface is wrinkled especially towards the former cell corner region. (c) Polymer infiltrated delignified wood composites with an additional fiber-matrix interface illustrated in red.

### 5.4.1. FVC

Increasing the FVC to maximum values for optimizing performance represents a major challenge in traditional unidirectional composite fabrication.\textsuperscript{132} The theoretical maximal FVC in continuous fiber reinforced composites is 70\% and practically approximately 63-65\%.\textsuperscript{3} The limit originates from the need of a certain minimal matrix thickness between fibers\textsuperscript{133} in combination with the incompressibility of synthetic reinforcing components such as glass fibers.\textsuperscript{3} Natural fiber composites rely on the same principle, meaning that stress-transfer between neighboring fibers is conducted through the matrix. However, without fiber deformation, the maximum fiber volume content of NFRPs is often even lower than the practical maximum for synthetic composites due to
their irregular shape and agglomeration into fiber bundles of varying diameter, which limits packing density. In contrast to synthetic fibers, however, plant fibers can be deformed. This property was utilized recently by Masania et al. for producing flax-polymer composites with FVCs up to 77%. In our case, we have manufactured delignified wood reinforced polymers with FVCs up to 85%, which by far exceed the limits of traditional composites design, thanks to the deformability of delignified wood fibers.

This deformability of natural fibers raises the question whether one could develop new high FVC concepts for plant-fiber composites that possess tight fiber-fiber interaction for stress-transfer, similar as for the here reported cellulose scaffolds. Tight interlocked fiber-fiber interfaces in plant-fiber composites necessitate high densification forces that are able to strongly deform the fibers. Challenges to produce such a highly densified matrix-free plant-fiber composites include the varying shape and size of fiber bundles, which could lead to non-unidirectionally aligned fibers. Additionally, waxes at the fiber surface could limit fiber-fiber adhesion requiring pretreatments such as alkali treatments that increase the amount of exposed cellulose on the fiber surface and enhance roughness to increase the fiber-fiber interlocking. Alternatively, one could consider delignification as pre-treatment to remove part of the cell-wall components and render the cells more flexible before simultaneous drying and densification. However, the structural integrity after delignification might be even more challenging for fiber-fabrics than for delignified wood and one could risk a complete disintegration during the delignification process. Although completely matrix-free plant fiber approach seems to be rather challenging at the moment, research in reducing the amount of matrix could optimize mechanical properties of natural fiber composites and result in even more sustainable materials.

5.4.2. Fiber - matrix interaction

In contrast to traditional fiber reinforced composites, delignified wood-polymer composites are interpenetrating composites. Interpenetration is obtained because both phases, the delignified wood scaffold and the matrix, are closely interconnected. The presence of matrix in lumina and pits creates a large fiber-matrix interface, which contributes to the mechanical properties of the composite. Such a synergistic strength improvement was also observed for transparent wood reported by Li et al. In transparent wood, the matrix PMMA penetrates lumina and cell walls. In contrast to this, epoxy did not penetrate into the cell walls of delignified wood. The reason for this is most likely the low porosity of the completely delignified wood cell wall after air-drying.
The resulting fiber-matrix interface in epoxy infiltrated delignified wood composites is wrinkled due to deformation of the cell wall upon densification. This mechanical roughening could contribute to an enhanced load-transfer between fiber and matrix.

An additional potential contributor to the observed matrix-stiffening effect is the interconnectivity of the matrix phase. The matrix spreads to neighboring lumina through pits in radial and transverse direction. This mechanical connections across the weaker out of plane direction is similarly done in z-pinning of composite laminates, so-called translaminar reinforcements, in order to enhance inter-laminar strength.\textsuperscript{136} These matrix connections through pits therefore could explain the enhanced bending properties and stiffness increase in tensile testing of matrix infiltrated delignified wood composites compared to the matrix-free counterparts. Tensile properties of infiltrated and densified cellulose composites are enhanced compared to matrix-free scaffolds and the tensile stiffness exceeds theoretical values calculated by the rule of mixtures. This suggests that more complex phenomena comprising an enhanced mechanical interlocking between neighboring fibers at higher fiber volume contents and the interpenetrating network substantially contribute to the stiffness of the composites. Highly densified epoxy-cellulose composites achieved very high tensile elastic moduli up to 70 GPa, where a maximum modulus of approximately 50 GPa, according to the rule of mixtures, would be expected. This non-linear increase in stiffness has been observed for an interconnected iron wire mesh reinforcement of aluminum alloys by Ganesh and Gupta\textsuperscript{137} and clearly demonstrates the importance of cellulose fibers interconnectivity for enhanced mechanical properties. Interlocking between neighboring fibers is increased upon densification, which could explain the non-linear increase in stiffness with density. This non-linear increase was reported in both, matrix-free and matrix-infiltrated cellulose composites. However, for matrix-free cellulose scaffolds, the increase in stiffness was less pronounced than for matrix infiltrated parts.

A drawback of matrix infiltrated materials compared to the matrix-free alternative is that the infiltration by synthetic non-biobased products makes the composites less sustainable. Additionally, vacuum infiltration of a hydrophobic matrix system needs to be conducted in dry state, because a wet scaffold would collapse under the applied vacuum. This, however, limits simultaneous shaping of the part as discussed in chapter 5.1. Thus, manufacturing of shaped, matrix-infiltrated components is rather difficult and needs to be conducted in multiple steps namely shaping in wet state, drying, infiltration and a final densification. Furthermore, infiltration
of bulk wood samples is limited due to the low flow-permeability of the scaffold and can only be conducted with very low-viscous infiltration resins. The infiltration of thermoplastic polymers or even bio-based matrices, which gain interest due to recyclability or damping properties, is not yet feasible with the current setup.

The need for a matrix has to be evaluated depending on the final application. Especially for optimizing mechanical performance or protecting the cellulose scaffold from humidity, an infiltration can be beneficial. Regarding efficiency and scalability, however, matrix infiltration into delignified wood is a limiting factor and will be discussed in the next chapter.
5.5. **Towards industrial scale**

5.5.1. **Densified cellulose materials**

Densified cellulose materials are produced in a relatively simple top-down approach that consists of delignification and densification. By that, one profits directly from the unidirectional alignment of cellulose fibers and the hierarchical structure of the scaffolds. Elaborate re-orientation and assembly steps, which are essential but often limit scalability in bottom-up approaches, are not needed in the production of delignified wood. In addition, delignification is a well-established process in the pulp and paper industry and structure-retaining delignification of wood potentially can be implemented in an existing plant. The densification step is also easily scalable and especially our newly developed open-mold vacuum processing technique, which allows for simultaneous densification and drying, is closely related to already existing vacuum processing methods that are industrially used in large-scale composite production.

We have investigated both, bulk wood and veneer processing methods. Bulk wood processing is especially appealing for research purposes due to the possibility to compare sample sets of identical growth ring patterns. Mechanical properties of wood vary largely depending on the location in the trunk. Therefore, scattering is minimized when sample sets of comparable properties like density and growth ring width are compared. However, the sample thickness is limited to approximately 1 cm. For thicker samples, the delignification time increases and needs to be repeated multiple times with new chemicals. Additionally, delignification gradients are more pronounced with increasing cross-section size. Therefore, regarding scalability of delignified wood-based materials, veneer processing is the method of choice. Delignification of veneers is less time consuming due to the smaller thickness and delignification inhomogeneities are less pronounced because mass transfer is enhanced. In addition, veneer-stacking promotes homogeneity of the final material compared to bulk materials, because density differences in individual layers are leveled out as similarly observed for engineered wood products. Furthermore, processing methods for veneer-based engineered wood products such as plywood are well-established in industry and can be adapted for the production of scalable delignified wood products.

A further advantage of veneer-based manufacturing represents the formability of veneers into very small radii of curvatures. The draping of delignified veneers onto porous molds of complex
shape followed by vacuum processing allowed the production of densified shaped parts, which was not possible to achieve for bulk material. The possibility to dry delignified veneers for interim storage or shipping is another advantage. Dry, non-densified delignified veneers could act as so-called prepgs, which are handled in dry state and can be re-hydrated and shaped into the final composite part. This re-shaping is possible due to the moisture triggered reversible interlocking mechanism in delignified wood, which was investigated in the second article.

A drawback of veneer-based techniques compared to bulk wood processing is the weak adhesion between delignified wood veneers, which results in delamination and necessitates the application of a binder. A water-based binder as demonstrated by using starch in the third paper would be the best option as it can be easily applied in wet-state and is bio-based. Starch is currently used as an adhesive in the paper industry for laminated paper products, to improve surface quality or for providing internal sheet strength and is the third most prevalent component by weight in papermaking after cellulose fiber and mineral pigments. Advantageous are its relatively low cost, the biodegradability and that it is derived from a renewable resource. To protect the material from moisture ingression, hydrophobic coatings or hydrophobic gluing systems are needed.

5.5.2. Delignified wood reinforced polymers

Bulk wood samples were used for better comparability of mechanical properties but also because the infiltration of delignified wood needs to be conducted in longitudinal direction in order to utilize the open path consisting of lumina and pits, which is eased if the cross section is large. However, the rather low permeability of dry delignified wood limits the maximum sample length to approximately 10 cm and therefore scalable veneer-based processing methods are highly desired.

Possible strategies for veneer-based composite manufacturing comprise stacking of polymer and delignified veneers followed by densification as similarly conducted in compression resin transfer molding (CRTM) for fiber reinforced composites manufacturing. However, a full infiltration throughout the veneers is very challenging, because the tight fiber-fiber connections prevent an infiltration-path surrounding the fibers as utilized in traditional CRTM. Potentially, a full penetration of the resin into the veneers is not even needed and a polymer that simply acts as
Delignified wood-based materials have a great application potential, for example in replacing glass fiber reinforced components for structural application in the automotive industry or in aviation. Regarding mechanical properties, the matrix-infiltrated version certainly has great potential but they still face some challenges when it comes to scalability. But also the matrix-free version possesses remarkable tensile properties, is bio-based, recyclable and biodegradable and could therefore contribute to more sustainable materials in the future. However, for a full evaluation of the potential, further investigation and optimization need to be conducted and suggestions for further research development are given in the outlook.
6 Outlook

The novel concept of densified delignified materials extends the research fields of wood and natural fiber reinforced composites and is aiming for improved mechanical performance compared to traditional plant fiber- and glass fiber reinforced composites. Differences like the interconnected character of fibers result in advantages over traditional composite architectures but also cause new challenges ranging from full mechanical characterization to the final manufacturing of products.

Research topics that need to be explored in the future for a thorough understanding of the new material comprise:

1. Mechanical characterization of the matrix-free and matrix infiltrated cellulose scaffolds to enhance understanding of the mechanics on all length-scales with a special focus on the interlocked fiber-fiber interface
2. Chemical and mechanical interface modifications to increase stress-transfer at the fiber-fiber interface
3. Manufacture of hybrid composites to optimize mechanical properties, to manufacture matrix-infiltrated composites in a scalable approach or to protect the material from moisture ingestion

For a successful implementation of delignified wood-based structural components in load-bearing applications, a detailed understanding of mechanical properties needs to be gained at all length scales parallel and perpendicular to the fiber direction. Single fiber tensile testing and micromechanical investigation on tissue level combined with macroscopic tensile and bending testing could help in understanding mechanical properties from the micro- to the macro-scale. Such a detailed understanding at all length-scales not only is important to understand the materials mechanical behavior but also to provide valuable input parameters for modeling.

Especially, the chemical and physical nature of the interlocked fiber-fiber interface and its effect on mechanical properties in fiber direction but also in transverse direction is barely understood but very critical for potential future applications. Transverse and out-of-plane properties are generally rather weak in anisotropic composite materials and therefore are often limiting factors in the design of high-performance structures. Delignified wood-based materials, however, possess
Outlook

Interlocked structures, which might be favorable for transverse properties of the material. Potentially, such interlocking concepts could also be transferred to other materials as suggested for plant fiber reinforced materials in chapter 5.4.1.

**Interface modifications** resulting in stronger fiber-fiber connections might push the limits of mechanical performance further. Possible strategies might include crosslinking of cellulose fibers, a process that is well known in the textile industry, or a fibrillation to potentially enhance the mechanical interlocking and strengthen the fiber-fiber interface as already discussed in chapter 5.2. Apart from that, optimized densification processing, e.g. by tailoring the molds, could potentially allow for achieving an even higher fiber volume content than reported in this thesis.

**Hybrid systems** as already reported for synthetic fibers and natural fibers potentially help to achieve a better combination of properties. Weak bending properties of delignified wood based materials would for example be compensated by using a high-compression strength fiber such as glass fibers in the compression-loaded region. Hybrid approaches could cover the use of various fibers in one component but also lay-ups with alternating matrix infiltrated- and non-infiltrated regions potentially lead to interesting properties and could be produced with scalable methods. The introduction of tough interlayers for example would provide high interlaminar fracture toughness or hydrophobic layers could reduce moisture ingression. Furthermore, hybrid systems would offer the possibility to include functionality into the composite part, for example by the use of a conductive polymer as interlayer, which would provide additional functionality to the end user.

A transition away from expensive glass, aramid or carbon fibers towards cheap and low density natural fibers is already in progress and can be complemented by delignified wood materials. Key important characteristics of materials used for automotive applications are the low price, recyclability and low weight combined with high specific mechanical properties. Thermal stability, moisture sensitivity, acoustic- or damping properties need to be considered, which still need to be analyzed for densified delignified wood in future studies. Further research needs to be conducted in order to promote the material and to compete on an industrial scale with other well established but less eco-friendly materials.
“[...] Wooden aeroplanes are under a cloud at the moment. However it would take a brave man to prophecy that they will never come back. One never can tell where wood will turn up next.”

_The new science of strong materials._

James Edward Gordon, 1991149
Appendix 1: Supplementary material to Delignified and Densified Cellulose Bulk Materials with Excellent Tensile Properties for Sustainable Engineering

Figure S1. Force-densification curve for a high force densified sample (a) and tool distance-time curve (b) for the stepwise densification procedure.

Figure S2. Mass and volume change as a result of the delignification procedure. A mass reduction of approx. 40 % and a volume loss of approx. 20 % are caused by the delignification. The mass and the volume of the native samples are set to 100 %.
Figure S3. SEM images of earlywood (a) and latewood (b) of densified native wood. Cracks in the cell walls are visible in the latewood cell walls.
Appendix 2: Supplementary material to Tunable Wood by Reversible Interlocking and Bioinspired Mechanical Gradients

**S1.** FTIR spectra of native, delignified, partially delignified latewood and partially delignified earlywood in the spectral range from 1800 to 900 cm\(^{-1}\). The characteristic lignin peaks at 1593, 1463, 1509 cm\(^{-1}\) (aromatic skeletal vibration) and 1264 cm\(^{-1}\) (guaiacyl ring breathing with CO stretching) (Schwanninger, 2011\(^{[1]}\)) are present in native wood and disappear upon delignification. Partially delignified wood shows lignin signals mainly in the latewood region, whereas the earlywood is completely delignified.

**S2.** Bioinspiration from trees on macro level (branch hole) and on micro level (wood ray)

**S3.** SEM images of the superhydrophobic TiO\(_2\)/PDMS coating on a delignified veneer surface (left) and zoom into regions of interest (middle, right).
S4. Contact angle measurements of native, delignified and delignified/superhydrophobic wood measured after $t = 0$ min and $t = 10$ min. The contact angle on native and delignified wood changes with time, whereas the droplet on the superhydrophobic surface keeps its shape.

S5. XRD pattern of native, delignified and native- and delignified magnetic wood. The characteristic crystalline cellulose peaks appear at 16.3, 22.2 and 34.4° (Park, 2010[2]). Maghemite ($\text{Fe}_2\text{O}_3$) or magnetite ($\text{Fe}_3\text{O}_4$) show characteristic peaks at 30.2, 35.5, 43.3, 57.4 and 62.8° (Schimanke et al., 2000[3]).
S6. Representative TGA curves for native, native magnetic, delignified and delignified magnetic wood. A weight gain of approximately 15% was obtained upon magnetization.
Appendix 2: Supplementary material to Tunable Wood by Reversible Interlocking and Bioinspired Mechanical Gradients

S7. (a) Magnetization behavior of native, delignified and delignified/densified magnetic samples and (b) susceptibility in longitudinal, tangential and radial direction. (c) SEM images of longitudinal cuts of native magnetic wood. (d) SEM images of delignified magnetic wood. (e) Shaped, magnetic, superhydrophobic wood, which is attached to a magnet. (f) Functional gradient material showing a higher magnetic moment and higher density on the right side (3 layers) than on the left side (1 layer).
Supplementary methods

<table>
<thead>
<tr>
<th></th>
<th>dimensions $r \times t \times l$ [mm$^3$]</th>
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<th>$2^{nd}$ delignification time at 80 °C [hours]</th>
</tr>
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<tr>
<td>bulk</td>
<td>100 x 10 x 20</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>bulk (thin)</td>
<td>100 x 5 x 20</td>
<td>6</td>
<td>4</td>
</tr>
<tr>
<td>veneer delignified</td>
<td>150 x 90 x 0.9 150 x 90 x 1.5</td>
<td>6</td>
<td>-</td>
</tr>
<tr>
<td>veneer partially delignified</td>
<td>150 x 90 x 0.9</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>cubes</td>
<td>5 x 5 x 5</td>
<td>6</td>
<td>-</td>
</tr>
</tbody>
</table>

Table S1: Delignification time according to the sample dimensions. Bulk samples were delignified a second time after exchanging the reaction solution.

Preparation of specimens with varying fiber volume content
Thin bulk samples (conditioned at 95% RH, 20 °C) were unidirectionally stacked and densified to a thickness of 5 mm using a closed mold following our previously established protocol.[4] Adhesive (Loctite Purbond HBS309) was applied in between the individual layers on the very top and bottom part of the samples, in order to avoid shear movements between layers in the clamped regions during mechanical testing. The test region was free of adhesive to ensure a matrix/adhesive independent characterization of the mechanical properties. Beech tags (2 mm thick) with an angle of 45 ° were glued to the grip section to avoid damage upon clamping in the universal testing machine.

Superhydrophobization
TiO$_2$ (Titanium (IV) oxide, anatase, <25 nm in size), Trichloro (1H, 1H, 2H, 2H-perfluorooctyl) silane (CF$_3$(CF$_2$)$_3$CH$_2$CH$_2$SiCl$_3$, PFOTS) were purchased from Sigma-Aldrich (Buchs SG, Switzerland). Polydimethylsiloxane (PDMS, Sylgard 184) and the corresponding curing agent were obtained from Dow Corning (Auburn, MI, USA). Tetrahydrofuran (THF, ≥99.0%) was supplied by VWR International (Zurich, Switzerland). All chemicals were used as received. The reaction protocol was adapted from Tu et al., 2016.[5]

In short, TiO$_2$ (1 g), THF$_r$ (60 ml) and PFOTS (0.5 ml) were mixed in a 150 ml beaker. The mixture was stirred at 65°C for 4 h under constant stirring and then dispersed with an ultrasonicator for 10 min. The PFOTS-modified TiO$_2$ particles were then collected by centrifugation and finally re-dispersed in 60 ml THF for further use. PDMS precursor (1 g) was dissolved in THF (30 ml) under magnetic stirring. PFOTS-modified TiO$_2$ nanoparticles were then dispersed in the PDMS solution under ultrasonication for 20 min to obtain solution A. PDMS curing agent (0.1 g) dissolved in THF (15 ml) results in solution B. Just prior to the coating treatment, solution A and B were mixed under ultrasonic dispersion for 20 min to form the PDMS/TiO$_2$ coating solution. The delignified wood samples were dipped into the coating solution for 10 seconds and dried at 65°C for 30 min. This procedure was repeated 3 times and the coated samples were then cured at 65°C for 5 h.

Magnetization
In situ magnetization of native and delignified wood cubes (5 x 5 x 5 mm$^3$) was conducted via coprecipitation of ferric and ferrous ions to obtain iron oxide particles as described in detail by Merk et al., 2014.[6] Prior to modification, the samples were dried at 65 °C and a Teflon tape was tied around the wood samples to keep their structural integrity during modification. The following
two solutions were prepared for the modification: Solution A: Ferric and ferrous chloride suspension with a fixed molar ratio of 2:1 with the concentrations 1.32 mol l⁻¹ ferric chloride (FeCl₃) and 0.66 mol l⁻¹ ferrous chloride (FeCl₂). Solution B: 25 ml of 25% aqueous ammonia was added to 400 ml deionized water.

The samples were vacuum infiltrated with solution A 3 times for 6 h. The samples were afterwards transferred to solution B for having a rapid addition of excess ammonia and remained in the solution for 24 h. Magnetic samples were washed with deionized water after the treatment until a neutral pH value of the washing solution was reached.

**Microtome and Ultramicrotome Cutting**

Sample cross-sections analyzed by light-microscopy (Olympus BX51) and AFM (JPK Instruments AG) were prepared using a rotary microtome (Leica Ultracut, Germany). Additionally, samples used for AFM measurements and shaped samples embedded in epoxy (Epofix) were cut using an ultramicrotome (Reichert-Jung Ultracut, Germany) with a diamond knife (Diatome).

**Atomic Force Microscopy (AFM)**

AFM imaging was performed on a Nano Wizard 4 (JPK Instruments AG, Germany) at 20 °C and 65% relative humidity.

*In situ* measurements of the cell corner of delignified spruce (Figure 2) were conducted in a petri dish filled with 10 mL of unstirred deionized water in contact mode. Cantilevers with a silicon probe and a nominal spring constant of 0.3 N m⁻¹ (CONTR, Nano world, resonance frequency 15 kHz) were used. The 10 x 10 µm² images were obtained at a line scan rate of 0.7 Hz and set points between 1 and 6 nN with a resolution of 512 x 512 pixels. AFM images of the cell corner before and after the submersion in water were acquired using the same imaging parameters.

The measurements of densified cell walls (Figure 3) were conducted in the quantitative imaging mode with a resolution of 256 x 256 pixels and a scan size of 20 x 20 µm². A noncontact cantilever (NCHR, Nano World, resonance frequency 320 kHz) with a silicon probe was used with a set point of 60 nN, z-length of 100 nm and a pixel time of 12 ms. The thermal noise method was used for calibration of the cantilever. Images were processed with the JPK image processing software (JPK Instruments AG).

**Water content**

The gravimetric water content of the locked, intermediate and morphing state was calculated by dividing the mass of water in the conditioned sample by the mass of the oven-dry sample. The mass was measured after conditioning at 20 °C/65% RH (locked state), 20 °C/95% RH (intermediate state) and after delignification and washing for obtaining the water content in wet (morphing) state. Samples were oven dried at 103 °C for obtaining the dry mass. 3 samples per condition were tested.

**Tensile testing**

Tensile tests were performed on a universal testing device (Zwick Roell, Germany) equipped with a 100 kN load cell. Conditioned specimens (25°C 65% RH) with the dimensions of 100 x 5 x 10 mm³ were tested with a span length of 36 mm, and the displacement was measured with a travel sensor with an initial length of 20 mm. The tests were conducted at 20 °C and 65 % relative humidity and a speed of 5 mm min⁻¹ and 6 samples per condition were tested.
Scanning Electron Microscopy (SEM)
Samples were coated with a sputter coater (CCU-010, Safematic). A Pt-Pd (80/20) coating of ~6 nm thickness was applied and the samples were analyzed with a Hitachi SU 5000 equipped with a SE detector.

Contact angle measurements
Static contact angles (CAs) were measured with the sessile drop method on tangentially cut wood veneers (native, delignified, modified). A Drop Shape Analyzer-DSA100 (Krüss GmbH) was used at ambient condition with a water droplet volume of 8 µl. The contact angle was determined immediately after contact and in constant time intervals up to 10 minutes. Time intervals of 80 s were used for the native and the superhydrophobically treated delignified wood. For delignified wood, the interval was set to 12 s in the beginning.

Vibrating sample magnetometry
The magnetic hysteresis was measured with a MicroMag 3900 Vibrating Sample Magnetometer (Princeton Measurements Corporation). The applied magnetic field was ranging from -10 kOe to 10 kOe in 100 Oe steps and an averaging time of 100 ms.

Kappabridge
A KLY-2 inductive susceptibility bridge (AGICO) was used to measure the susceptibility and the anisotropy of low-field magnetic susceptibility at a magnetic field of 200 A m⁻¹.

Fourier Transform Infrared Spectroscopy (FTIR)
Wood veneer surfaces were analyzed with an ATR-FTIR spectrometer (Bruker Tensor 27). Baseline correction (concave rubber band) and normalization (min/max) of the obtained spectra was conducted in the software OPUS.

X-ray Diffraction (XRD)
XRD diffraction patterns were recorded for native and delignified spruce and for the magnetically modified native and delignified wood cubes. The surface of a longitudinal cut was analyzed using a PANalytical Empyrean diffractometer (Almelo, Netherlands) in the Bragg-Brentano mode with a Cu Kα radiation. A 2θ range of 5 - 80° was measured. For magnetic samples, a nickel filter was used to reduce the fluorescence. The diffraction curves were normalized and smoothened in OriginPro 2016.

Thermogravimetric analysis (TGA)
Wood cubes were cut into small pieces with a razor blade and were analyzed with a TGA under nitrogen atmosphere. A TGA Q50 (TA Instruments) with a heating rate of 10 C min⁻¹ (30-800 °C) was used for the measurement.

References
5. K. Tu, L. Kong, X. Wang, J. Liu, Holzforschung 2016, 70, 1039.
Supplementary figures

**Figure S1.** Native wood (left) and partially delignified wood (right). Partially delignified bulk wood shows a decreasing lignin content from the inside to the outside of the sample.

**Figure S2.** Schematic profile through the VARI infiltration setup prior to densification. Three delignified wood samples (blue) surrounded by breather (white) are placed on a metal plate. The flow mesh (yellow) guides the resin from the inlet to the front side of the samples. Spiral tubes are attached at the ends of inlet and outlet and a vacuum bag (green) covers the whole setup.
Figure S3. Densification curves of dry cellulose scaffolds (65% RH) of densities varying between 0.27 and 0.38 g/cm$^3$. Densification of earlywood occurred at relatively low stress (below 2 MPa) whereas much higher stress was required for the densification of latewood.

Figure S4. Shows false-colored (a) polished cross section of a DWRP latewood displaying cracks between neighboring cells and (b) cross section of earlywood showing cracks within the cell wall close to the fiber-matrix interface. (c) False-colored SEM and (d) AFM images of the fiber-matrix interface in latewood showing the wrinkled interface on both, macro- as well as on the nano-scale.
Figure S5. Specific tensile modulus vs. specific tensile strength of wood, DW, DWRP, GFRP compared to literature values.
Figure S6. (a) Representative tensile stress-strain curves of GFRP, DWRP, DW and wood. (b) Light-microscopy images of the fracture after bending in DWRP and GFRP. (c) Bottom and (d) top part of the sample after bending testing.
Table S1: Tensile stiffness, tensile strength and density of measured composites and reference literature values.

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<tr>
<th>Material</th>
<th>$E$ (GPa)</th>
<th>$\sigma_t$ (MPa)</th>
<th>$\delta$ (kgm$^{-3}$)</th>
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<td>wood</td>
<td>10.59 ± 1.60</td>
<td>79.28 ± 13.87</td>
<td>0.41 ± 0.03</td>
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<td>GFRP 25 %</td>
<td>19.69 ± 2.53</td>
<td>277.49 ± 81.14</td>
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<td>GFRP 50 %</td>
<td>38.11 ± 3.66</td>
<td>469.46 ± 95.88</td>
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<td>13.56 ± 5.15</td>
<td>109.85 ± 13.10</td>
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<td>28.78 ± 4.92</td>
<td>220.50 ± 30.01</td>
<td>0.99 ± 0.05</td>
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<td>161.59 ± 34.69</td>
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<tr>
<td>DWRP 50 %</td>
<td>34.26 ± 3.96</td>
<td>300.64 ± 77.39</td>
<td>1.31 ± 0.01</td>
</tr>
<tr>
<td>DWRP 70 %</td>
<td>52.01 ± 11.56</td>
<td>504.69 ± 108.05</td>
<td>1.32 ± 0.07</td>
</tr>
</tbody>
</table>

Table S2. Flexural stiffness, flexural strength and density of measured composites and reference literature values.

<table>
<thead>
<tr>
<th>Material</th>
<th>$E$ (GPa)</th>
<th>$\sigma_b$ (MPa)</th>
<th>$\delta$ (kgm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>wood</td>
<td>10.48 ± 1.20</td>
<td>77.85 ± 7.89</td>
<td>0.40</td>
</tr>
<tr>
<td>GFRP 25 %</td>
<td>17.73 ± 2.47</td>
<td>455.39 ± 63.72</td>
<td>1.51 ± 0.05</td>
</tr>
<tr>
<td>GFRP 50 %</td>
<td>36.94 ± 2.83</td>
<td>872.02 ± 71.14</td>
<td>1.85 ± 0.05</td>
</tr>
<tr>
<td>DW 25 %</td>
<td>16.49 ± 2.88</td>
<td>63.32 ± 9.36</td>
<td>0.56 ± 0.05</td>
</tr>
<tr>
<td>DW 50 %</td>
<td>19.27 ± 5.57</td>
<td>85.63 ± 22.67</td>
<td>0.99 ± 0.05</td>
</tr>
<tr>
<td>DWRP 25 %</td>
<td>19.55 ± 2.94</td>
<td>200.05 ± 16.61</td>
<td>1.17 ± 0.06</td>
</tr>
<tr>
<td>DWRP 50 %</td>
<td>35.84 ± 3.52</td>
<td>356.27 ± 29.46</td>
<td>1.30 ± 0.02</td>
</tr>
<tr>
<td>DWRP 70 %</td>
<td>46.76 ± 4.36</td>
<td>421.63 ± 37.20</td>
<td>1.32 ± 0.07</td>
</tr>
</tbody>
</table>
Appendix 3: Supplementary material to Delignified Wood-Polymer Interpenetrating Composites Exceeding the Rule of Mixtures

Supplementary Methods

Euler’s critical load for buckling:

\[ P_{cr} = \frac{\pi EI}{(KL)^2} \]  

(1)

Where E represents the modulus of elasticity of column material, I represents the area moment of inertia of the cross section of the column, K represents the column effective length factor and L the length of the column.

Critical load for buckling of earlywood compared to latewood with the assumptions that \( E_{LW} = E_{EW} \):

\[ \frac{P_{EW}}{P_{LW}} = \frac{I_{EW}L_{EW}^2K_{EW}^2}{I_{LW}L_{LW}^2K_{LW}^2} = \frac{b_{EW}L_{EW}^3L_{EW}^2K_{LW}^2}{b_{LW}L_{LW}^3L_{EW}^2K_{LW}^2} = \frac{b_{EW}L_{EW}K_{LW}^2}{b_{LW}L_{LW}K_{EW}^2} \]

Assuming, that the average width-ratio of earlywood to latewood cell walls \( \frac{b_{EW}}{b_{LW}} \) is \( \frac{1}{2} \) and that the average height of earlywood to latewood \( \frac{L_{EW}}{L_{LW}} \) is \( \frac{1}{3} \):

\[ \frac{P_{EW}}{P_{LW}} = \frac{1}{6} \frac{K_{LW}^2}{K_{EW}^2} \]

Which means that \( \frac{1}{6} \)th of the latewood densification force is needed for an average earlywood cell densification under the assumption, that earlywood and latewood buckle in the same mode \( (K_{EW} = K_{LW} = 1) \).

However, under the assumption that earlywood buckles in a higher buckling mode \( (K_{EW} = 0.5) \), earlywood buckling load increases to \( \frac{2}{3} \)th of the latewood buckling load.

\[ \frac{P_{EW}}{P_{LW}} = \frac{1}{6} \frac{1}{0.25} = \frac{2}{3} \]
Appendix 3: Supplementary material to Delignified Wood-Polymer Interpenetrating Composites Exceeding the Rule of Mixtures

**Rule of mixtures upper bound:**\(^1\)

\[
E_c = f E_f + (1 - f) E_m
\]

Where \(E_c\) represents the modulus of elasticity of the composite, \(E_f\) represents the modulus of elasticity of the fiber, \(E_m\) is the modulus of the matrix and \(f\) represents the volume fraction of the fibers.

**Halpin Tsai equation:**\(^1\)

\[
E_c = E_m \left( \frac{1 + \zeta \eta f}{1 - \eta f} \right)
\]

\[
\eta = \frac{E_f}{E_m} - 1 \frac{E_f}{E_m} + \zeta
\]

Where \(\zeta\) is a parameter that depends on the geometry of the filler as follows:

\[
\zeta = \frac{2 l}{d} \text{ for the longitudinal modulus}
\]

\[
\zeta = 2 \text{ for the transversal modulus}
\]

Where \(l/d\) is the aspect ratio of the filler.

**References**

Bibliography


Curriculum Vitae

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Professional Experience

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Development Engineer
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Project lead for: Development of a carbon fiber reinforced flat-cable for elevation application
Publications

1. Frey, M., Schneider, L., Masania, K., Keplinger, T. and Burgert, I. *Delignified Wood-Polymer Interpenetrating Composites Exceeding the Rule of Mixtures*; ACS Applied Materials & Interfaces; 2019

2. Frey, M., Schneider, L., Zirkelbach, M., Dransfeld, C., Masania, K., Keplinger, T. and Burgert, I. *Densified Cellulose Materials and Delignified Wood Reinforced Composites*; ICCM22; 2019

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8. Keplinger, T., Frey, M., Burgert, I.; *Versatile Strategies for the Development of Wood-Based Functional Materials*; Proceedings of SPIE; 2018


Patents

Teaching Experience

Teaching
1. Laboratory Course “Holz und Holzwerkstoffe – Mikromechanik” for Civil Engineering Bachelor Students (2019)
2. Laboratory Teaching Assistant (ETHZ): Chemistry Lab Course for Materials Science Bachelor Students (2013)

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Awards
2. Heinzel Mondi Sappi Award in the category “Cascaded use of wood” for the paper “Delignified densified bulk wood with excellent tensile properties for sustainable engineering”. Graz, Austria. (2018)

3. Talk prize – 1st runner up at “Meet and share your research day” at ETHZ. Zürich, Switzerland. (2017)


**Conference Contributions**


Adobes-Vidal, M., **Frey, M.**, Keplinger, T., Burgert, I., *New Strategies for High Resolution Imaging of Plant Cell Walls by Atomic Force Microscopy (poster presentation)*, Cell Wall Meeting, Cambridge, United Kingdom, 2019


Grönquist, P., **Frey, M.**, Thybring, E.E., Burgert, I; *Measuring hydroxyl accessibility of Delignified Wood by Hydrogen-Deuterium Exchange*, 1st European Symposium on Sorption Science, Vienna, Austria 2018

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Keplinger, T., **Frey, M.**, Burgert, I; *Versatile Strategies for the Development of Wood-based Functional Materials*, SPIE, Denver, Colorado, United States 2018

**Frey, M.**, Widner, D., Segmehl, J.S., Casdorff, K., Keplinger, T., Burgert, I; *Delignified and Densified Cellulose Bulk Materials*, Paper and Biorefinery, Graz, Austria 2018 (invited)

**Frey, M.**, Widner, D., Segmehl, J.S., Casdorff, K., Keplinger, T., Burgert, I; *Densified Cellulose Scaffolds for a New Class of Composite Materials*, Bio-Inspired Materials, Potsdam, Germany 2018

**Frey, M.**, Keplinger, T., Biffi, G., Zirkelbach, M., Tu, K., Hirt, A.M., Burgert, I; *Lightweight morphing structural cellulose materials with bioinspired mechanical and functional gradients (poster presentation)*, EMPA Peer Review Day, Dübendorf, Switzerland 2018

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Erklärung


Zürich, 25.11.2019

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