Delignification and Ionic Liquid Treatment of Wood toward Multifunctional High-Performance Structural Materials

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ABSTRACT: Wood-based multifunctional materials with excellent mechanical performance are increasingly considered for sustainable advanced applications due to their unique hierarchical structure and inherent reinforcing cellulose phase orientation. Nonetheless, a wider multipurpose utilization of wood materials is so far hampered because of constraints arising from scalable functionalization, efficient processing, facile shaping as well as natural heterogeneity and durability. This study introduces a multifunctional all-wood material fabrication method relying on delignification, ionic liquid (IL) treatment, and pressure-assisted consolidation of wood. Structure-retaining controlled delignification of wood was performed to enable direct access to the hierarchical cellulose assembly, while preserving the highly aligned and thus beneficial wood structural directionality. As a following step, the obtained biobased scaffold with an increased porosity was infiltrated with an IL and heat-activated to partially dissolve and soften the cellulose fiber surface. Samples washed with water to remove IL exhibited pronounced isotropic flexibility, which upon combined compression and lateral shear allowed the fabrication of various 3D shapes with adjustable fiber architecture. The obtained very compact and totally additive-free all-wood materials were extensively characterized, revealing superior mechanical performance, and gained multifunctionality compared to native wood.

KEYWORDS: all-wood materials, ionic liquid dissolution, natural fiber interpenetrating composites, delignification, wet 3D shaping, wood modification

INTRODUCTION

Multifunctional high-performance lightweight structural materials of exceptional mechanical properties are in high demand in our technologized society. During the last years, by mimicking structure–function relationships in natural materials, a broad range of synthetic lightweight hierarchical materials was designed. In particular, natural building blocks such as nanocellulosic materials [cellulose nanofibrils (CNFs)] have gained interest as structuring and reinforcing elements in novel composite systems. Such cellulosic materials are predominantly obtained from plants within disintegration processes leading to the loss of the original multihierarchical three-dimensional structure of precursor natural materials and especially wood. Moreover, for a wide utilization of CNFs, certain challenges arising from high energy-demanding disassembly processes and difficulties in composite system preparation with beneficial parallel alignment of CNFs should be overcome. Even though great progress regarding CNF alignment using a sophisticated microfluidic system has recently been achieved, enabling the formation of high-performance macroscale fibers, it still remains challenging to fabricate CNF composites with high fiber directionality.

Approaches that allow retaining the native hierarchical structure of wood and thus profit from its unique microstructural organization and fiber directionality appear to be promising manufacturing and functionalization alternatives. Besides, nowadays, large volumes of wood at low cost are readily available, not to mention that structural optimization during the natural growth process favors adequate mechanical performance of wood with a lightweight design. However, certain restrictions need to be resolved for a wider utilization of wood-based materials in high-end structural applications. These mainly include the heterogeneity of the natural material, leading to a low reliability in terms of mechanical properties. Another limitation is that it is rather challenging to modify the very compact wood cell walls with good control on the functionalization efficacy unless complex chemistries are utilized.

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The top-down approach that allows the utilization and modification of the inherent hierarchical structure of wood has recently become an appealing alternative to add novel specific functionalities to broaden the application areas of wood, while preserving its sophisticated structure. These include transparency,8 electrical properties,9–11 magnetism,12,13 biosorption,14 stimuli-responsiveness,15 supercapacitance,16 and oil–water separation features.17,18 Transformation of wood into a high-performance engineering material has recently been demonstrated involving structure-preserving delignification followed by densification steps.19,20 An interconnected cellulose phase with an impressive stress transfer even without the addition of a matrix was achieved after full delignification and drying of wood, which facilitated neighboring fibers to come into close contact with each other.21 Moreover, transparent and anisotropic films with aligned cellulose fibers were manufactured directly from wood following a similar method.22 Alternatively, excellent mechanical performance was achieved by Song et al. after densification of partially delignified wood (DLW) by hot pressing, where the remaining lignin acted as a matrix.23 Delignification of carefully preselected wood followed by phenolic resin infiltration and densification resulted in very stiff, strong, and moisture-stable wood-based composites.24 However, relatively long infiltration times combined with the need of raw material preselection reduce scalability of such approach.

Another alternative to manufacture high-performance functional biomaterials is an all-cellulose composite approach, where cellulose is utilized both for reinforcement and for the matrix. In such single-polymer systems, intact highly crystalline cellulose is embedded into a matrix of regenerated cellulose.25–27 Therefore, extremely high mechanical performance of the fabricated materials is expected because of profound interfacial adhesion between chemically identical components. All-cellulose systems are typically manufactured either (1) by combining untreated cellulose with completely dissolved cellulose, which upon the subsequent coagulation (regeneration) step forms the matrix phase, or (2) by partial surface dissolution of the preassembled cellulose-based structures followed by coagulation to form a matrix phase.

A broad range of the nonderivatizing (which do not alter the cellulose chemistry and thus not diminishing its excellent biodegradability) direct dissolution systems have been utilized for cellulose, such as lithium chloride/N,N-dimethylacetamide (LiCl/DMAC), 4-methylmorpholine N-oxide (NMMO·H2O), NaOH–water (without additives or with urea), and ionic liquids (ILs).28,29 In this context, ILs are appealing agents as they are able to dissolve all wood components30 (cellulose, hemicellulose, and, to some extent, lignin), meaning that they can be utilized to fabricate all-lignocellulosic materials. For example, an all-wood composite material from hinoki wood can be utilized to fabricate all-lignocellulosic materials. For instance, preparative and drying of wood, which facilitated neighboring fibers to come into close contact with each other.21 Moreover, transparent and anisotropic films with aligned cellulose fibers were manufactured directly from wood following a similar method.22 Alternatively, excellent mechanical performance was achieved by Song et al. after densification of partially delignified wood (DLW) by hot pressing, where the remaining lignin acted as a matrix.23 Delignification of carefully preselected wood followed by phenolic resin infiltration and densification resulted in very stiff, strong, and moisture-stable wood-based composites.24 However, relatively long infiltration times combined with the need of raw material preselection reduce scalability of such approach.

In this work, partly aiming at addressing some of the challenges discussed above, we propose a simple and upscalable manufacturing process of multifunctional high-performance structural materials from wood. This is achieved by combining delignification, IL treatment, and densification, as schematically illustrated in Figure 1. Structure-retaining delignification was first performed (following processes well adapted from pulp and paper industry) to increase the pore volume, while preserving the fiber directionality of wood. DLW was next impregnated under ambient conditions with an IL, heated to partially dissolve the fiber surface, washed with water to remove the IL, and, finally, densified while heated. The chemical composition of fabricated wood structures was carefully characterized using Fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR) spectroscopies, whereas the morphological details were examined by scanning electron microscopy (SEM). Furthermore, several physical properties were evaluated in order to evidence the multifunctional character, that is, mechanical performance,
optical properties, surface hardness, rub-wear resistance, and gas moisture, and grease permeabilities.

**EXPERIMENTAL SECTION**

**Delignification of Wood.** Birch wood plies (Metsä Wood) with a density of $\sim$530 kg/m$^3$ and a thickness of 1.5 ± 0.1 mm were used as a raw material. Wood plies (with dimensions of $\sim$10 cm $\times$ 15 cm and a dry weight of $\sim$250 g) were delignified at 80 °C under continuous stirring using 1 wt % sodium chlorite (NaClO$_2$, Sigma-Aldrich) in 10 mM acetate buffer solution (5000 mL, pH 4.6). The extraction steps (12 h each) were repeated two times. Afterward, delignified samples were carefully washed and kept overnight in Milli-Q water.

**Treatment with an IL.** Wet DLW was placed in an IL, 1-ethyl-3-methylimidazolium acetate, [Emim]OAc, (>95% purity, purchased from IoLiTec Ionic Liquids Technologies GmbH, Germany) for a given period of time both at atmospheric pressure and under vacuum (≤15 mbar). Afterward, slightly drained to remove excess of IL, infiltrated wood was placed on a metal plate covered with baking paper and heated in an oven at 95 °C either for 1 or 6 h. Next, to remove the IL from the activated samples, they were kept in Milli-Q purified water at room temperature until washing water became colorless. Purified samples were then cased between Sefar PETEX 07-1/2 fabric and stacked between blotting papers. Finally, the formed pile was dried in a hot press under 5 MPa at 100 °C overnight. Dried samples were then stored at 23 °C and 50% RH. Wet DLW was exposed to hot pressing only and was used as a reference.

**3D Shaping of Treated Wood.** The press forming process using closed metal molds was used to prepare 3D shapes of various geometries and curvatures from modified wood. Wet treated wood was placed on a female mold, and the pin-guided male mold was placed on top so that it does not touch the sample as the metal springs were placed between the molds. Afterward, the molds were pressed at 100 °C until the sample dried. Prior to forming, the samples were covered with Sefar fabrics to facilitate the moisture transport from the system.

**Characterization.**

- **Gravimetric Analyses for Moisture Evaporation from IL-Impregnated Wood.** The evaporation rate of moisture from IL-impregnated DLW was assessed with a computer-controlled gravimetric moisture analyzer (Ohaus MB45, NJ, USA). The temperature was set to 95 °C, and the sample size was approximately 6 $\times$ 6 $\text{cm}^2$. Prior to measurement, samples were pressed between blotting papers using 4 kg weight for 10 s. All measurements were at least duplicated.

- **Nitrogen content** of IL-impregnated DLW was measured using a Fisons Instruments EA 1108 elemental analyzer. The average values of at least three replicates of each sample type were used to calculate the IL content.

- **Scanning Electron Microscopy.** The cross sections of delignified and modified wood materials were analyzed with a Merlin field emission scanning electron microscope (Carl Zeiss NTS GmbH, Germany). The samples cross sections were prepared using a Hitachi IM4000 broad ion beam cross-sectional cutter. Before SEM characterization, all samples were gold/palladium sputter-coated (Leica EM ACE200) at 30 mA for 30 s ($\sim$2 nm thickness). The delignified sample was dehydrated (step by step) using first pure ethanol, then a 1:1 (volume ratio) mixture of ethanol and acetone, and, finally, pure acetone. Each step was repeated three times.

- **Chemistry by FTIR–ATR and Solid-State NMR.** Wood delignification and IL-facilitated partial dissolution were verified with a Thermo Scientific Nicolet iS50 FTIR spectrometer with an attenuated total reflectance (ATR) diamond (Thermo Scientific, USA). All spectra were collected in the absorption mode in the 400–4000 cm$^{-1}$ wavelength range from 32 scans with a resolution of 4 cm$^{-1}$. The $^{13}$C cross polarization (CP) magic angle spinning (MAS) NMR measurements were performed using an Agilent DD2 600 NMR spectrometer with a magnetic flux density of 14.1 T, equipped with a 3.2 mm T3 MAS NMR probe operating in a double-resonance mode. Samples were packed in ZrO$_2$ rotors, and the MAS rate in experiments was set to 10 kHz. A total of 14,000 scans were accumulated using a 1.3 ms contact time and a 5.0 s delay between successive scans. Protons were decoupled during acquisition using SPINAL-64 proton decoupling with a field strength of 80 kHz. 90° pulse durations and Hartmann–Hahn match for CP were calibrated using a glycine. The spectra were processed using TopSpin 3.5 software. The changes in the crystallinity of the wood after delignification and partial dissolution with the IL were estimated from signal areas of the cellulose C$_6$ carbon signals originating from crystalline (89.0–84.4 ppm) and noncrystalline (84.4–77.3 ppm) regions. Signal areas were determined by integration.

- **Tensile Testing.** Mechanical properties of fabricated samples were investigated with an MTS 400/M (MTS Systems, USA) tensile tester using a 1 kN load cell at 10%/min strain rate and 25 mm span. Each sample was cut into a strip (5 mm $\times$ 50 mm) and conditioned at 50% relative humidity (RH) and a temperature of 23 °C for at least 24 h. Wet tensile strength was measured after keeping the samples in deionized water for 5 days. The average values of at least five replicates are reported.

- **Optical Properties.** Diffusive transmittance of modified wood was measured with a Cary 5000 UV–vis–NIR spectrophotometer (Agilent Technologies) involving an integrating sphere (DRA 2500, Agilent) at a scan rate of 600 nm/min and a data interval of 1 nm, between 800 and 300 nm.

- **Surface Hardness.** Hardness (defined as a material’s resistance to permanent indentation) of prepared samples was assessed using a Shore tester according to the ASTM D2240 type A and type D scales, where the A scale is used for softer materials, while the D scale is for harder ones. All samples were conditioned for at least 24 h at 50% RH and a temperature of 23 °C. At least 10 replicates of each sample type were measured (test duration was 15 s), and the average values are reported.

- **Rub-Wear Resistance.** The resistance of surfaces to rubbing abrasion was evaluated with a Taber rotary platform abrasion tester (model 5131) using an H-18 Calibrate abrading wheel and 500 g load. Characteristic rub-wear action is produced by contact of a test sample against the sliding rotation of two abrading wheels. The weight loss method was used to evaluate the test results by calculating the Taber wear index (rate of wear), which is the loss in weight (in milligrams) per thousand cycles of abrasion. The lower the wear index, the better the abrasion resistance quality of a material. All samples were conditioned for at least 24 h at 50% RH and a temperature of 23 °C. Three replicates of each sample type were measured, and the average values are reported.

- **Gas, Moisture, and Grease Permeability.** Air permeability of the samples was investigated in accordance with the ISO 5636-3:2013(E) Part 3: Bendtsen method using an L&W air permeance tester. At least 10 replicates of each sample type were measured (test duration was 15 s), and the average values are reported. The oxygen transmission rate (OTR) through the samples was determined with an oxygen permeation analyzer (model 8101, Systech Instruments Ltd, UK) according to standard ASTM D3985. The tests were carried out using 100% oxygen as a probing gas at 23 °C and 50% RH applying metal masks with a test area of 5 cm$^2$. Four duplicate measurements were carried out. Oxygen permeability (OP) was then calculated as follows: by multiplying OTR value by the sample thickness of the sample and then dividing by sea level pressure

\[
\text{OP} = \frac{\text{OTR-thickness}}{\text{oxygen partial pressure difference}}
\]

Water vapor transmission rates (WVTR) were determined gravimetrically using a modified ASTM E-96 B procedure, the ‘dry cup method’. Samples with a test area of 30 cm$^2$ were mounted on circular aluminum cups (68–3000 Vapometer EZ-Cups; Thwing-Albert Instrument Company) containing anhydrous CaCl$_2$ (0% RH). The cups were stored under test conditions of 23 °C and 50% RH and weighed periodically until a constant rate of weight reduction was attained. In this test, the 50/0% RH gradient (the driving force for water molecules to diffuse within a material) was used. Four duplicate measurements were carried out. Water vapor permeability (WVP) was then obtained as follows: by multiplying WVTR by the sample
thickness and then dividing by the water vapor difference across the film

\[
\text{WVP} = \frac{\text{WVTR-thickness}}{\text{saturated pressure} \cdot \Delta \% \text{RH}}
\]  

(2)

Resistance to grease penetration was assessed according to the method reported previously.\textsuperscript{32} Briefly, tested samples (50 mm × 50 mm) were sandwiched between the transparent glass plate (bottom) and circular blotting paper of diameter 30 mm (top). "Oil Red O" (1-{4-(xyllylazo)xyllyl}azo)-2-naph-thol, 1-{3,5-dimethyl-4-(2,5-dimethylphenylazo)phenylazo}-2-naph-thol, Solvent Red 27, Sigma-Aldrich; 200 μL)-dyed oil was pipetted onto the blotting paper followed by placing a 50 g weight (diameter 30 mm) onto the formed pile. Grease permeation through the sample was detected using an image scanner (300 dpi, 24-bit color) through the glass plate. Five parallel measurements with periodic image scanning were carried out for 136 h.

RESULTS AND DISCUSSION

In the first step, wood was chemically treated with sodium chlorite to partially remove lignin. Protocol established in our previous investigation was employed, which showed that lignin content was partly reduced (from ∼25% to ∼10%) in natural wood upon delignification, whereas only minor reduction in hemicellulose contents was observed.\textsuperscript{33} Figure 2 shows the cross sections of wood before and after delignification, which indicates that the structure and organization of wood cell walls are well preserved after partial lignin removal. Moreover, the delignification process leads to a higher porosity of the wood, thus facilitating the chemicals assess to the cellulose fibers.

In the following step, DLW was infiltrated with an IL, [Emim]OAc, by placing wet samples in fresh IL solution under vacuum (≤15 mbar). Three different infiltration times (0.5, 1, and 6 h) were tested and distinguished on the basis of IL impregnation inside the wood structure. Figure 3a illustrates somewhat lower initial water content levels of samples that were infiltrated with an IL for a longer time, which could possibly be attributed to water evaporation during the vacuum-assisted IL infiltration process (low pressure ≤ 15 mbar was utilized). Nevertheless, after heating at 95 °C for 60 min, the moisture content was similar for all samples. Figure 3b shows that an IL loading of ∼50% with respect to sample mass could be achieved and did not differ much within the infiltration time. Furthermore, the level of IL impregnation was the same when infiltration was performed at atmospheric pressure. This implies that osmotic pressure due to different ionic strengths in wet samples and [Emim]OAc is decisive for sufficient IL impregnation even under ambient conditions. Overall, these observations might be of great practical importance keeping in mind industrial implementation for two reasons: (1) The wet substrate can be used, which saves costs and time arising from wood sample drying. Moreover, conventional wood drying might lead to the hornification effect: as wood shrinking during drying is facilitated because of partial lignin removal, this, in turn, will cause pore collapse in the wood structure, thus hindering chemical penetration for further functionalization. Implementation of drying techniques such as solvent exchange or freeze-drying could mitigate this problem but their low-cost realization at industrial scale is challenging. (2) IL impregnation at the ambient environment because typically vacuum is utilized for successful chemical impregnation inside the porous wood structure, which again leads to additional costs.

Defect-free IL-impregnated DLW was further heat-treated in an oven at 95 °C for 1 and 6 h to partially dissolve the surface of cellulose fibers. As apparent from Figure 3c, no changes of the sample surface morphology could be detected after 1 h; however, the sample became somewhat brownish. In contrast, heat treatment for 6 h leads to more extensive sample darkening with visually detectable, translucent, and viscous spots indicating sample dissolution.

In the subsequent step, the treated wood was washed with deionized water to remove the IL. This resulted in a flexible wood of gel type, as is visualized in Figure 3d,e, by bending the treated wood. It is likely that during heat treatment, the surface of cellulose fibers was first partially dissolved (surface of the cellulose fibers became easily accessible because of lignin removal) and then consequently coagulated (regenerated), resulting in a gel-type layer onto the intact inner fiber structure. This hypothesis could be confirmed by surface hardness measurements, Figure 3f, where the wood surface became softer with longer heat treatment with an IL. Moreover, the formed gel-type layer decreased interactions (acted as a lubricant) between neighboring fibers, leading to plastic-like mechanical behavior of IL-treated wood, as validated in Figure 3g.

Interestingly, IL-treated wood shows isotropic flexibility unlike DLW, which can only bend in a transverse direction to fiber orientation, Figure 3e. These observations could also suggest effortless designing of wood-based objects with complex geometries and various (3D) shapes that fully preserve fiber alignment. Lignin (acting as an adhesive between the wood fibers) partial removal in the structure-preserving delignification process enabled slight mobility of the fibers relative to each other. Meanwhile, the gel-type layer formed at the fiber interface further facilitated water-triggered rearrangement of the fiber network in a controllable manner. Drying of the assembled fiber network accompanied by compressive and shear deformations promotes hydrogen bonding and enables mechanical interlocking between fibers. As a result, strong interfaces are created with close contact between fibers. 3D-shaped objects fabricated from treated wood are presented in Figure 4. Besides trays suitable for packaging applications, shaped wood can also be utilized as an acoustic resonator for guitars.

Tensile tests of the manufactured samples validate that prominent material properties can be obtained by pressure-assisted densification and IL treatment, while maintaining the hierarchical structural integrity of the wood, as demonstrated by representative stress–strain curves presented in Figure 5a. Significant mechanical property improvements were attained upon compression of DLW (∼260 MPa), while only a moderate increase in tensile strength was observed upon densification of native wood (∼120 MPa compared to ∼70
MPa, for reference, unmodified wood). The lignin removal promoted cell collapse upon compression (Figure 5g), most likely because of suppression of the transverse rigidity of the wood cell walls, which is also reflected in higher density of pressed delignified wood (DLWP) (~1170 kg/m³) compared to ~1060 kg/m³ for pressed original wood (OWP), Figure 5b. As a result, the voids between the cell walls in native wood, Figure 5e, disappeared, resulting in a more pronounced cell folding compared to OWP (Figure 5f). Upon IL treatment, cell walls appear strongly interconnected with each other after heat-assisted compression of DLW, Figure 5h,i, leading to a highly consolidated structure. Density of DLW subjected to IL treatment for 6 h (sample IL-6 h) reached 1335 kg/m³, whereas IL treatment for 1 h (sample IL-1 h) resulted in a density of 1250 kg/m³. However, despite higher density of sample IL-6 h, superior mechanical properties were achieved.
accompanied by regenerated cellulose sample IL-1 h compared to of the modi
network formation within the adjacent decrystallization of cellulose I, and extensive hydrogen bonding solubilizes, leading to the opening of the polymer structure, penetration, the surface of individual cellulose spectra. It has been previously documented that upon IL (sample IL-1 h) did not reveal any signi
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Meanwhile, absorbance attributed to C−OH and C−CH deformation vibrations, C−O stretching, CH$_2$ wagging, C−O− C asymmetric stretching (1000−1300 cm$^{-1}$), and O−H stretching (2600−3500 cm$^{-1}$) in samples OW and DLW confirms maintaining of the cellulose I structure typically present in unmodified wood.$^{37,38}$ IL treatment of DLW for 1 h (sample IL-1 h) did not reveal any significant changes in spectra. It has been previously documented that upon IL penetration, the surface of individual cellulose fibers swells and solubilizes, leading to the opening of the polymer structure, decrystallization of cellulose I, and extensive hydrogen bonding network formation within the adjacent fibers.$^{39}$ Consequently, it could be concluded that IL treatment of DLW for 1 h was sufficient only to solubilize and swell the outer surface of individual fibers, which upon regeneration (washing with water) resulted in a more compact structure and density increase (the hydrogen bonded fiber−fiber joints are accompanied by regenerated cellulose−cellulose joints$^{40}$). In contrast, upon longer IL treatment for 6 h (sample IL-6 h), FTIR spectra illustrate changes in regions associated with crystallinity and hydrogen bonding. Indeed, peaks at 1022−1015 and 895−990 cm$^{-1}$ (C−O stretching vibrations at the C6 position of the anhydroxyranose unit) shift and at 2600−3500 cm$^{-1}$ (O−H stretching) broaden, indicating partial loss in crystallinity upon cellulose I conversion to cellulose II. Moreover, the entire absence of characteristic lignin peaks was observed. Therefore, it is reasonable to assume that lignin low-molecular fractions remaining after delignification were dissolved and further removed upon IL treatment and the subsequent water washing step. Finally, wood became deacetylated, as was apparent from a loss of intensity in a strong peak at 1730 cm$^{-1}$, most likely because of [Emim]OAc-induced deacetylation of xylan.$^{31}$ In line with FTIR findings, NMR measurements did not reveal characteristic peaks of regenerated cellulose$^{42}$ after IL treatment for 1 h (sample IL-1 h) and no significant change in the carbon signal of the wood was observed,$^{43}$ Figure 6b. After longer IL treatment for 6 h (sample IL-6 h), C6 moved to lower chemical shift, indicating the formation of cellulose II, and the intensity of the crystalline C4 peak decreased, implying the loss of the cellulose I structure. As a result, the calculated crystallinity of cellulose has decreased by 11%, whereas crystallinities for OW (35%), DLW (38%), and DLW treated with IL for 1 h (38%) do not differ much within the experimental error. Despite improved bonding, a decrease in crystallinity might be responsible for lowering the mechanical performance of DLW treated with IL for 6 h.

The densified wood swells extensively after keeping the samples in deionized water for 5 days, Figure 5c, whereas OW showed an increase of only 3.3% in thickness, with only a modest drop in tensile strength ($\sim 68$ MPa compared to $\sim 72$ MPa for natural wood in an ambient environment), Figure 5d. Interestingly, despite pronounced swelling of compressed OW ($\sim 50$%), tensile strength remained practically unchanged, whereas a more drastic decrease in strength properties and an increase in thickness swelling were prominent for lignin-free samples. Nevertheless, tensile strength of wet, delignified, and IL-treated (for 1 h) sample is still two times higher than that of natural wood in an ambient environment. Furthermore, tensile properties in the transverse (perpendicular to fiber orientation) direction were also enhanced, Figure 7a. Remarkably, IL-treated for 1 and 6 h delignified wood samples have tensile strength values almost 1.5 and 2 times higher ($\sim 18$ and $\sim 24$ MPa, respectively) compared to pressed delignified wood, DLWP, ($\sim 12$ MPa) and $\sim 7$ and $\sim 9$ times higher, respectively, when compared to unmodified wood ($\sim 2.6$ MPa). It is most likely that better interconnection between fibers is achieved for DLW treated with the IL for a shorter time ($\sim 370$ MPa for sample IL-1 h compared to $\sim 220$ MPa for sample IL-6 h).

The difference in the mechanical performance of the samples could be explained in terms of chemical properties of the modified wood. The lignin partial removal is evidenced by the absence of the lignin-specific IR bands (1590, 1501, and 1452 cm$^{-1}$ due to aromatic skeletal vibration, and 1230 cm$^{-1}$ due to guaiacyl ring breathing with C−O stretching), Figure 6a.

Figure 4. Photographs of 3D-shaped treated wood of various geometries. In addition to formed trays suitable for packaging applications, treated wood can also be utilized as an acoustic resonator for guitars. On the picture, Versoul Resosun 6 String Acoustic Resonator Guitar; photo credit: Versoul Ltd.
upon pressing the regenerated jell-type layers. As apparent from Figure 7c−f, delignified and unmodified (original) wood exhibited extensive cell wall cracking upon densification, whereas more uniformly compressed cells with almost no
detectable cracks in the structure could be observed for IL-treated DLW. Therefore, superior mechanical properties of IL-treated samples could be attributed to uniform stress transfer in the material upon loading. Moreover, it is worth highlighting that the fabricated samples were totally additive-free (composed entirely from wood components), and hence, only the interactions within the aligned cellulose fibers were decisive.

The comparison in Figure 8a validates that not only stiffer all-wood materials (compared to unmodified wood) but also those with an enhanced work of fracture (derived from the tensile tests) could be produced by densification of IL-treated wood. It is also worth noting that the strain at failure was relatively high for all modified samples, in particular, the specimens that were compressed after IL treatment for 1 h show superior performance for all measured mechanical properties. A desirable combination of strength, toughness, and stiffness can be found in several biological systems, but it remains a challenge to attain such performances in the engineering materials. There are only few examples in the literature that have demonstrated superior mechanical parameters for the developed wood-polymer composites at the macroscale. Hence, the presented approach clearly confirms the advantage of preserving the natural hierarchical fiber structure in wood with simultaneously enhanced fiber interface bonding with an IL treatment for the preparation of biobased macroscopic materials rather than embedding disassembled natural fibers in a polymer matrix to fabricate composites, which eventually possess lower stiffness and strength values.
Apart from the enhanced mechanical properties, manufactured wood demonstrated improved material’s resistance to surface deformation (hardness), Figure 8b, and resistance to rubbing abrasion (rub-wear surface resistance), Figure 8c. Furthermore, because highly packed structures were achieved, processed wood efficiently prevents air, oxygen molecules, grease, and water vapor permeability through the sample. For example, compared to commercial cellophane and LDPE films, which were measured as a reference, the water vapor permeability of delignified, IL-treated, and compressed wood (∼790 g × μm/m² × day × kPa) was lower than that for cellophane films (∼12,500 g × μm/m² × day × kPa) but ∼19 higher compared to that of the synthetic polymer, such as tested LDPE films (∼40 g × μm/m² × day × kPa),52 which is still impressive, given the hydroscopic nature of the fabricated material.

Interestingly, densely packed and hydrophilic samples were also effective in retarding the permeability of oxygen through the wood structure under moderate atmospheric conditions (50 RH %), as is evident from Figure 8h. As fabricated samples were totally additive-free, highly packed crystalline domains present in the original fibrillar structure of cellulose I were efficiently connected with regenerated cellulose. Moreover, oxygen molecules (low polarity) display only weak interactions with hydroxyl groups (high polarity) of modified wood. All these impede the oxygen molecules to permeate through the delignified, IL-treated, and compressed wood.

Additionally, the fabricated wood has a certain degree of transparency, Figure 8e,f. An achieved diffusive transmittance of 53% at 600 nm (40% at 550 nm) indicates partial interface removal within the delignified, IL-treated, and compressed wood. Indeed, Snell’s law states that light is diffacted when it passes through an interface,47 and the diffraction angle is proportional to the refractive index mismatch between the two media. Thus, by compressing the delignified and IL-treated wood, we obtained an optically less heterogeneous material by tailoring the refractive index mismatch between the polymer components in wood (light absorbing lignin was partly removed) and by improved interconnections within the fabricated sample (IL treatment facilitated interface removal), which are critical for optical performance.

Overall, wood modification protocol presented here clearly demonstrates the benefits of preserving the natural fiber hierarchical structure for the fabrication of biobased engineer-
ing materials without the utilization of any adhesives. Hence, a substantial step toward high-performance functional applications based on lignocellulosic renewable materials is shown. Moreover, the fabricated material has a certain degree of gas, oxygen, grease, and water vapor barrier features and transparency, which in combination with facile formability (possibility of desired 3D shape fabrication) could benefit different applications. Furthermore, composed entirely of wood components, the developed system is fully biodegradable, which certainly is an additional asset for sustainable applications.

## CONCLUSIONS

The high-performance material was developed from natural wood in a step-by-step process involving partial lignin removal, IL-facilitated cellulose fiber surface dissolution followed by coagulation in water, and subsequent temperature-assisted densification (compression). As a result, compact structures with a particular fiber-folding pattern due to embedding of the undissolved fibers into a matrix of regenerated cellulose were formed. In addition, wet shaping of processed wood allows shape tuning in a predictable and desired fashion, which offers the possibility to transform wood into a versatile engineering material with remarkable mechanical parameters. The manufactured wood material had a tensile strength of ~370 MPa, tensile stiffness of ~46 GPa, work of fracture of 7.8 MJ/m² in the longitudinal direction, and almost 10-fold tensile strength improvement in the direction perpendicular to fiber orientation. Additionally, the matrix-free wood demonstrates limited permeability of gas, grease, and water vapor because of the dense and well-packed structure and has a certain degree of transparency. This approach demonstrates the feasibility to fabricate the multifunctional material from wood and, thus, has vast relevance in an emerging field of sustainable high-performance materials.

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### Notes

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