Wood-Gelatin Bio-Composite Membranes with Tunable Flux

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Abstract

Wood is an attractive bio-resource for the production of functional materials, as it provides a complex hierarchical structure with unique properties. It is particularly promising for membrane applications due to its aligned micropores, which enable directed flow of liquids. However, wood-based functional membranes often rely on the combination of wood with non-eco-friendly compounds or production methods. Furthermore, the performance of such membranes is pre-determined by wood's intrinsic porosity, which cannot be regulated.

Here we present a green sustainable bio-composite material for an application as tunable membrane by the combination of beech wood and gelatin. Investigation of the composite material with electron microscopy, X-ray microtomography, as well as FTIR- and Raman-spectroscopy shows, that the gelatin is distributed inside the cell lumina as thin film at the cell wall/lumen interface. The thickness of this film is tunable by the feed gelatin concentration. Furthermore, the gelatin forms meniscus-like structures that block vessels and hence impede capillary water transport through the wood structure. As a result, the flux of wood-gelatin composite membranes is tunable by both the sample thickness and the gelatin loading.

The composites offer straightforward separation of wood and gelatin by immersion in warm water. Therefore, separate reuse or recycling of the constituents is possible. Due to its adjustability and eco-friendliness, the developed bio-composite provides a sustainable and versatile platform for membrane applications.

Keywords: Bio-based materials, Natural resources, Protein, Tunable membrane, Biodegradable, composite separation

Introduction

Bio-based materials from renewable resources are intensively investigated in today's research, as they are CO₂-storing, often bio-degradable, and offer a wide variety of properties and functions. Therefore, they can contribute to the necessary transformation towards a circular economy. Natural materials that possess a hierarchical structure are of particular interest, as they can realize unique and often anisotropic properties by a sophisticated composition of their molecular or nano-sized building blocks.¹⁻² Hence, tedious bottom-up assembly routes can be omitted by using such natural materials as scaffolds for the development of functional

materials.³ Wood is a natural fiber composite with an anisotropic hierarchical structure across several length-scales. It is abundant, cheap, relatively light-weight, and can be processed in large amounts by established techniques.⁴ This makes wood a promising green resource for the development of new materials. Therefore, several wood-based functional materials have been developed recently, which make use of its anisotropic properties.⁵

Wood is particularly suited for membrane applications due to its natural structure. Its anisotropic micropores ensure directed transport of liquids with high throughput and low pressure drop.⁶ In general, hardwoods, such as the beech wood used in this study, mainly contain two different kinds of micropores: fiber lumina and vessel lumina. Both are tubular channels in the growth direction of the tree and essentially the vessel lumina serve as transport pathways for water in the living plant.⁷ Fiber cells form shorter channels with smaller diameters, whereas vessels form longer channels with larger diameters. By using wood with this natural porosity as a membrane material, tedious bottom-up synthesis routes, which are normally used for polymers or other precursors, can be omitted.

Membranes made from natural wood are able to sieve micrometer-sized colloidal pollutants from water^{6, 8-10} and to separate oil-water mixtures,¹¹ without the need of any modification. In addition, wood has been chemically modified to create wood-based membranes with novel characteristics. The resulting wood-based hybrid or composite membranes were applied for heavy metal scavenging,¹² oil-water separation,¹³⁻¹⁴ catalysis,¹⁵⁻¹⁶ water purification,¹⁷⁻²⁰ energy storage,²¹ or cell cultivation.²²

These modifications rely on chemical alteration of the wood material. They introduce functional compounds to the wood structure, such as metal and metal oxide particles^{15, 17, 20} or organic small molecules and polymers.¹²⁻¹⁴ Additionally, some approaches require wood delignification prior to the modification to tune certain characteristics, such as porosity or flexibility.^{13-14, 22}

All of these approaches strongly focus on imparting specific functions to the wood. However, the performance of a membrane does not depend only on its selectivity, but also on the membrane's flow-through characteristics. The flux of wood-based membranes, and hence their performance, are determined by the porosity of the wood. Thereby, the porosity is pre-determined by the wood species and its particular anatomy, resulting in a fixed flow-through behavior. In general, wood-based membranes exhibit very high flux values due to their pore structure and overall high porosity, which can be unfavorable for certain applications.^{16, 23}

It is in particular a problem if hardwoods are used that exhibit an extensive vessel network, which provides unhindered flow through the structure as the pore length exceeds the thickness of the membrane.⁶ Concomitantly, there is little knowledge yet about influencing the flow-through behavior of wood-based membranes and controlling the flux of wood-based membranes has never been investigated.

For synthetic membranes, which are mostly polymer-based, the flow-through is determined by tuning the material's porosity upon membrane synthesis.²⁴ This is not possible for wood-based membranes, as the porosity is pre-determined by the used wood species. Hence, modification of the wood porosity is necessary. Possible approaches are the filling of the pores with synthetic polymers or polymer hydrogels, by chemical coupling of a polymerization starter or polymerizable double bonds to the cell walls, followed by *in situ* radical polymerization.²⁵⁻²⁶ Depending on the process, the polymers form a thin layer on the cell wall/lumen interface, or fill entirely the wood micropores. This results in changed properties on the macroscopic level, such as impeded water penetration. However, the resulting wood-polymer hybrid materials were not applied as membranes and the implications of the modifications for membrane processes remain unclear. Moreover, the tuning of the polymer localization and particularly of the amount of filled pores or the thickness of the polymer layer at the cell wall/lumen interface is challenging due to the uncontrolled radical polymerization process. Furthermore, these

approaches rely on solvent-based chemistry as well as the introduction of petroleum-based and non-biodegradable polymers to the wood structure. Hence, the resulting hybrids cannot be considered green materials.

In this work, we present a green approach towards eco-friendly wood-based membranes with tunable flux by the modification of wood with the biological hydrogel gelatin. This polypeptide is a natural low-cost and abundant industrial by-product, which is soluble in water and exhibits temperature-responsive gelation behavior.²⁷ The gelatin forms a hydrogel layer with tunable thickness at the cell wall/lumen interface, as well as vessel-clogging structures, which are randomly distributed throughout the samples. These micro-structural features lead to a tunable liquid flux of the composite material when applied as a membrane. The combination of these natural resources in a simple and entirely water-based process creates a green bio-composite material that is applicable as a tunable membrane.

Results and Discussion

Figure 1: (A) Schematic illustration of the top-down approach for the production of a green bio-composite membrane. Firstly, wood, with structure and porosity facilitating an application as membrane material, is taken from a tree. Secondly, the wood is functionalized with gelatin. (B) Schematic illustration of the modification of beech wood with gelatin and the microstructure of the resulting composite.

A green approach towards the production of a tunable bio-composite membrane in a two-step top-down process is illustrated in Figure 1 A. Cylindrical beech wood samples were vacuum-impregnated with aqueous gelatin solutions of different concentrations and subsequently dried. The resulting wood-gelatin composites combine the intrinsic hierarchical structure of wood with the natural hydrogel, which covers the cell wall-lumen interface and forms vessel clogging structures (Figure 1 B).

The weight percent gain (WPG) of the wood samples during impregnation can be controlled by the feed gelatin concentration (Figure 2 E). The WPG increases with increasing feed gelatin concentration (= gelatin loading) from 4.4 % for a feed gelatin concentration of 30 mg*ml⁻¹ to a maximum of 25.3 % for a gelatin concentration of 300 mg*ml⁻¹ (Table S1 provides a detailed overview of the WPGs depending on the feed gelatin concentrations). Note that there is a certain amount of water, which is bound to the gelatin and contributes to the weight gain, as the samples were stored in a controlled climate (20°C, 65 % r.h.).

We analyzed the microstructure of the wood-gelatin composite by scanning electron microscopy (SEM) and micro X-ray tomography to evaluate the localization and morphology of the gelatin inside the wood structure. Fiber lumina are visible as smaller black areas in the SEM micrographs of the cross sections (perpendicular to tree growth direction) and as smaller horizontal channels in the micrographs of the longitudinal-tangential cuts (parallel to tree growth direction) in Figure 2 A and B (examples indicated by the letter F). Vessels are visible as bigger black areas in the micrographs of the cross sections and as broad horizontal channels in the micrographs of the longitudinal-tangential cuts (examples indicated by the letter V).

After gelatin impregnation, an additional thin layer becomes visible on the inner vessel surfaces, both in the cross sections and the tangential cuts. (Figure 2 A). At very high gelatin loading (300 mg*ml⁻¹) it occurs also within the fiber lumina of the wood-gelatin composites. The layer was red colored in the micrographs of the cross sections for better visualization. The tangential

cuts further show that the layer covers also the pits (indicated with the latter H). These pits connect neighboring vessels and guarantee liquid flow between them. The pits are well visible at low gelatin loadings and get increasingly covered, and hence less distinguishable, with higher gelatin loading. No such layer is visible in unmodified wood (Figure 2 B), indicating that it was introduced during the impregnation process.

The layer thickness depends on the gelatin loading. It varies from 0.9 μm at 30 $\text{mg}\cdot\text{ml}^{-1}$ to ca. 2.1 μm for a concentration of 100 $\text{mg}\cdot\text{ml}^{-1}$ and up to 3.5 μm for a concentration of 300 $\text{mg}\cdot\text{ml}^{-1}$ (Figure 2 D; Table S1 gives a detailed overview over the layer thicknesses). Therefore, varying the feed gelatin concentration enables a direct control over the layer thickness.

Figure 2: (A) Electron micrographs of wood-gelatin composites with various feed gelatin concentrations. The left images show cross sections, whereas the right images show longitudinal-tangential cuts. Representative vessels and fibers are indicated with the letters V and F, respectively. An additional layer is visible at the vessel walls, which gets thicker with increasing gelatin loading. For 300 $\text{mg} \cdot \text{ml}^{-1}$, the layer is also visible inside the fibers. The

gelatin layers were red colored in the cross section images. In the images of the longitudinal-tangential cuts, the layer is visible covering the pits (indicated with the letter H). (B) Electron micrographs of unmodified beech wood as reference. (C) Electron micrograph of a cross section of wood-gelatin composite showing clogged vessels (indicated with red arrows). The inset shows a clogged vessel with higher magnification. (scale bars depict 25 μm in A - C) (D) Graph of weight gain (black squares) and gelatin layer thickness (red triangles) plotted against the feed gelatin concentration (sample thickness: 5 mm). (E) Cube of wood-gelatin composite (100 $\text{mg}\cdot\text{ml}^{-1}$) reconstructed from micro X-ray tomography data. The red arrows indicate meniscus-like structures, which clog the vessels. The inset shows a magnification of such a structure (scale bars depict 50 μm for the cube and 10 μm in the inset).

Furthermore, the SEM micrographs show that some individual vessels are completely clogged (Figure 2 C). We performed X-ray microtomography on wood-gelatin composites to evaluate the three dimensional structure of the whole sample and to gain detailed information on the location and distribution of these clogging structures. Figure 2 E shows a cubic cutout that was reconstructed from the X-ray microtomography data. Figure S1 displays the X-ray microtomography image of an exemplary plane of the wood-gelatin composite. Solid (dense) structures appear bright, whereas the air-filled pores appear dark. The vessels are hence visible as dark vertical channels. In the wood-gelatin composite, white lines are visible, which span the vessels (Figures 2 E and S1, examples indicated with arrows). These meniscus-like structures are randomly distributed in the vessels of the wood-gelatin composites, whereas they are not visible in native wood (the videos V1 and V2 in the electronic SI show stacked X-ray microtomography images of the modified wood as well as the unmodified reference, respectively). The absence of meniscus-like structures in native wood indicates that they do not represent inherent wood structure features, such as scalariform perforations between

neighboring vessels. This leads to the conclusion that they were introduced during the gelatin impregnation and formed during the drying process.

The structural investigation by SEM was complemented by chemical analysis of the wood-gelatin composites with Fourier-transformed infrared spectroscopy (FTIR) and Raman microscopy. Infrared spectroscopy confirmed the gelatin infiltration into the wood structure. The FTIR spectrum (Figure 3 A) shows a gelatin characteristic amide I band at a wavelength of 1635 cm^{-1} and an amide II band at 1558 cm^{-1} , which are absent in the native wood spectrum.²⁸

Raman microscopy provides a spatially resolved analysis of the wood-gelatin composites. Hence, it was used to investigate the chemical composition of the layers within the vessels, which were observed by electron microscopy, to confirm that they are not part of the native wood structure. The visualized line in the SEM image (Figure 4 B) illustrates the Raman line scan measurement position. The measurement was conducted from the wood cell wall across the gelatin layer at the cell wall-lumen interface in direction of the green arrow (corresponding white light image provided in Figure S2). The Raman spectra presented in Figure 4 B were extracted from the line scan. Magenta spectra correspond to measurement positions within the cell wall and cyan spectra to the gelatin layer. Cell wall spectra show distinctive bands for wood constituents, such as bands at 1095 cm^{-1} and 1120 cm^{-1} , which are attributed to cellulose (C-O-C stretching vibrations of cellulose) and bands at 1598 cm^{-1} (ring deformation) and 1656 cm^{-1} (C=C stretching of the ethenyl moiety of coniferyl alcohol) characteristic for lignin.²⁹

Wood characterizing cellulose and lignin bands are absent in the cyan spectra, whereas bands at 1670 cm^{-1} and 1253 cm^{-1} occur, which are attributed to amide I and amide III vibrations. These are typical marker bands for polypeptide structures, such as gelatin.³⁰ The measurement confirms that the layer next to vessel walls, visible in SEM images, is gelatin and that there is no penetration into the wood cell wall.

Figure 3: (A) FTIR spectra of native beech wood (black) and wood-gelatin composite (red). The inset shows the region of interest at frequencies between 1800 cm^{-1} and 1500 cm^{-1} . The peak at 1635 cm^{-1} is the amide I peak and the one at 1558 cm^{-1} the amide II peak. These peaks are characteristic for gelatin and absent in the native wood spectra. (B) Raman spectroscopy measurements of wood-gelatin composites. Top image: schematic representation of the measurement position. A line scan (represented by the cyan and magenta line) was performed across the interface between wood cell wall and the proposed gelatin layer in the direction of the green arrow. For better visibility, a representative SEM image was used to illustrate the

position and direction of the line scan (scale bar: 20 μm ; see Figure S2 for the original measurement location and white light image). Bottom image: Raman spectra that were extracted from the line scan. Magenta plotted spectra, correspond to the magenta part of the line (wood cell wall region) and show characteristic peaks for the cell wall components cellulose (1377 cm^{-1} and 1095 cm^{-1}) and lignin (1598 cm^{-1} and 1656 cm^{-1}). These peaks are absent in the cyan spectra, which represent the cyan line part (proposed gelatin layer). These spectra show characteristic peaks for gelatin (1253 cm^{-1} and 1670 cm^{-1}).

The introduction of the gelatin to the wood structure changes the morphology of its micropore network. This causes a change in the liquid transport through the material and hence its permeability. We visualize this behavior qualitatively by the deferred uptake of a water droplet (Figure 4 A). A droplet, which was placed on the cross section of native wood, is immediately absorbed to the structure. In the case of wood-gelatin composite, however, the droplet remains on the surface of the sample and is not absorbed. This shows, that water penetration into the structure is decreased by the gelatin. We applied time-dependent contact angle measurements for a quantification of this behavior (Figure 4 B). This method enables the observation of the contact angle of a water droplet on the surface and its behavior over time. The time-depending water contact angle thus provides additional information about the penetration of the drop into the structure. On native wood, the contact angle (Θ) rapidly decreases in the first 30 seconds after the drop deposition due to absorption into the wood structure. The contact angle of water on wood-gelatin composite, in contrast, only slightly decreases from approximately 70° to 60° in the same amount of time.

These results show that water cannot readily penetrate the wood-gelatin composite, as it is possible for native wood. We explain this behavior with a blocking of the vessels as transport pathways by the gelatin (Figure 4 C). In native wood, the water from the droplet quickly fills

the vessels of the wood structure. Hence, the droplet volume decreases, leading to a decreased contact angle ($\Theta < \Theta_0$). In wood-gelatin composites, transport through the vessels is blocked, as the meniscus-like structures clog the vessels and the film on the vessel walls blocks the pits. Hence, when the droplet is deposited on the surface of the sample, air is trapped inside the vessels under the droplet. It cannot leave the vessels to the bottom, due to the gelatin structures and can also not exit the vessel to the top due to water's surface tension. Therefore, water cannot get into the vessels, resulting in constant drop volume and thus no change of the contact angle. The slight decrease of the contact angle over time is supposedly caused mainly by swelling of the gelatin and the wood. This is backed by the water uptake and swelling behavior of the wood-gelatin composites when immersed into water (Figure S3). Compared to native wood, the water-uptake and swelling are retarded. However, wood-gelatin composites eventually take up more water than native wood, due to the additional uptake of the gelatin. This shows that the water cannot penetrate the composites as quickly as native wood, due to hampered capillary transport, but is also not excluded from the structure.

Figure 4: (A) Photographs of a colored water drop on cross sections of unmodified native wood (left) and wood-gelatin composite ($120 \text{ mg} \cdot \text{ml}^{-1}$). The photo on the top shows the situation immediately after the drops were deposited, whereas the photo on the bottom shows the situation 10 s after the drops were deposited. (B) Plot of the time-dependent contact angles of water on cross sections of wood-gelatin composite ($120 \text{ mg} \cdot \text{ml}^{-1}$, black squares) and of native

wood (red circles), illustrating deferred water-uptake of wood-gelatin composites. (C) Schematic illustration of the proposed mechanism of capillary water transport into the structure of native wood and wood-gelatin composite. For native wood, the drop volume and thus the contact angle decrease due to capillary transport of the water into the vessels. In wood-gelatin composites, the capillary transport pathways through the vessels are blocked. Hence, water cannot get into the vessels, resulting in constant drop volume and contact angle.

The change in permeability causes deferred flux of wood-gelatin composite membranes. We tested the influence of the gelatin loading on the flux for three sample thicknesses (3, 5, and 7 mm). The customized set-up used for these measurements is shown in Figure S4. Its central element is a sample holder, which tightly fixes the cylindrical samples, allowing water flow only through and not around them. A constant water flow was initiated with a peristaltic pump. The flux was calculated from the increasing permeate mass, which was determined with a lab scale. Figure 5 shows the flux values for varying sample thickness and gelatin loading. Figure S5 gives a detailed overview of all results including standard deviations of the data.

Native wood without gelatin loading exhibited a constant flux for all three thicknesses, which was the maximum flux provided by the pump and is about $27000 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$. A control experiment with native wood of 70 mm thickness resulted in the same unhindered flow. This shows that beech does not provide significant resistance for the water flow in our setup, even at higher sample thicknesses. The flux is pre-determined by the wood species used and its porosity. It cannot be regulated for beech and even very thick membranes exhibit a very high flux. Concomitantly, thin wood-based membranes exhibit very high flux values even when softwoods are used that do not have wide and long vessels but solely contain a lot smaller and shorter pores.¹⁶ However, high flux values are not suitable for certain applications. In flow-

through catalysis, for example, a high flux results in too short contact times between catalyst and substrate, and hence lower catalytic efficiency.³¹

A completely different behavior is present for wood-gelatin composites, where the flux depended on the gelatin loading at each sample thickness. The thinnest samples (3 mm) exhibited the maximal flux of about $27000 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ for both 30 and $60 \text{ mg}\cdot\text{ml}^{-1}$. This indicates, that, similar to native wood, thin samples with low gelatin loading do not provide sufficient barrier to reduce the water flow. However, the flux decreased at each individual thickness with increasing gelatin loading. Accordingly, it also decreased at a fixed gelatin loading with increasing sample thickness. In our setup, we could therefore adjust the flux between very high values of about $27000 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ (3 mm, 30 and $60 \text{ mg}\cdot\text{ml}^{-1}$) and low values of about $26 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ (7 mm, $90 \text{ mg}\cdot\text{ml}^{-1}$).

The reason for this observation is the higher probability for a thicker sample that a vessel is clogged by gelatin and not available for water transport, as the clogging structures are randomly distributed in the structure. Furthermore, we suppose that a higher gelatin loading and hence a thicker gelatin layer on the vessel walls leads to a more effective blocking of the pits. Consequently, water flow between vessels is increasingly impeded for higher gelatin concentrations.

A wide variety of possible flux values is highly beneficial, as different applications require specific permeabilities. Flow-through catalysis, for example, profits from a lower flux and hence longer contact time of the reactants with the active membrane. For filter applications, in contrast, a higher flux is desirable.

Figure 5: Plot of the water fluxes through wood-gelatin composite samples and native wood. The flux is determined by both, the feed gelatin concentration and the sample thickness. It decreases with increasing gelatin concentration and with increasing sample thickness.

Unlike most composite materials, the wood-gelatin composites offer the possibility of facile separation of the components at the end of lifetime, by immersing wood-gelatin composites just in warm water (75 °C). The gelatin is water-soluble at elevated temperatures and is washed out of the wood structure. The samples lose the weight that they had gained during the impregnation with gelatin (Figure 6 A). Accordingly, the water used for separation contained gelatin after the process. The characteristic gelatin peaks at 1635 cm⁻¹ and 1558 cm⁻¹ are present in the FTIR spectra (Figure 6 B). This shows that the major part of the gelatin loading was removed from the wood structure by the simple separation procedure. The composite constituents can be

separated and regained easily, hence allowing for separate recycling of the wood and the gelatin. However, this behavior also implies that the material should not be used above a certain temperature to avoid washing out the gelatin. In contrast, no gelatin is washed out when the samples are likewise immersed in water at room temperature (Figure S6). This indicates that almost no gelatin leaches from the wood structure at room temperature, which coincides with the insolubility of gelatin at temperatures below 35°C.³²

The possibility of simple constituent separation is an important characteristic for a composite, as recyclability and the environmental impact of its degradation are central aspects for a circular economy. Conventional composite materials are hard to recycle, as their constituents cannot be easily separated.³³ This is the case particularly for wood-based functional materials, which are mostly wood-polymer or wood-mineral composites and hybrids. Wood and the functional agents are inseparably combined in these materials and there is no work yet that shows their separation.

Figure 6: (A) Plot of the sample weights before and after gelatin loading and after the separation procedure. The weight increases upon gelatin loading and decreases again after the separation procedure. This indicates that the gelatin is washed out during the separation process.

(B) FTIR spectrum of the gelatin separated from wood-gelatin composites (red) and of pure gelatin (black). Characteristic bands are present at 1635 cm^{-1} and 1558 cm^{-1} .

Conclusion and Outlook

We presented a novel approach for the green production of a sustainable bio-composite membrane material. The top-down approach is in stark contrast to conventional bottom-up membrane fabrication. The natural material wood acts as a promising membrane due to its anisotropic porous microstructure. The wood was modified with the biopolymer gelatin in an aqueous process to manipulate the material's microporosity for its use as a tunable membrane.

Characterization of the wood-gelatin composite showed that the gelatin is deposited in the wood pores as a thin layer at the cell wall/lumen interface. The thickness of this layer is controllable by the gelatin loading. Moreover, the gelatin forms meniscus-like structures that clog the vessels and are randomly distributed throughout the wood structure. As a consequence, the capillary transport pathways of liquid through the wood structure are blocked, leading to changed water permeability.

When applied as a membrane, the permeability of wood-gelatin composites depends on both the sample thickness and the gelatin loading. The flux decreases for both, increasing sample thickness and increasing gelatin loading. Hence, the flux can be tuned over a broad range from very high to low values. This makes the material attractive for a variety of different applications.

Regarding recyclability at the end of lifetime, the material constituents can be separated by immersion in hot water. The constituents can thus easily be regained and subsequently be reused. This is of special interest, if the gelatin contains further functionalization or scavenged compounds, which must not be discharged to the environment.

The gelatin broadens the range of potential future applications of wood-based membranes. It introduces multiple functional groups to the wood structure, due to its polypeptide nature. Hence, modification approaches are not anymore restricted to OH-groups as in native wood. Various chemical modifications of gelatin were presented, most of which make use of the amino groups of lysine, hydroxylysine, or the N-terminal amino acid.²⁷ Chemicals that can be bound to the gelatin by this route include organic anhydrides, halocarbons, cyanates, imides, and organic peroxides. Moreover, gelatin could be chemically modified prior to its introduction to the wood structure. This potentially enables homogeneous binding of functional molecules, omitting tedious impregnation procedures to bring the reaction solution inside the wood structure.

The broad range of possible flux values, the potential to further modify the gelatin inside the wood structure or prior to impregnation, and the straightforward separation and recycling of the constituents make the wood-gelatin composite an interesting material in the growing field of bio-based functional materials. In combination with various approaches for the development of wood-based membranes, which have been presented recently, it may contribute to the production of novel sustainable functional membrane materials.

Materials and Methods

Beech wood samples were cut from cylindrical sticks with a circular saw (diameter = 18 mm, heights = 3, 5, and 7 mm). The samples were cut from multiple sticks stemming from independent trees to account for the natural wood heterogeneity. All samples were stored under controlled climate conditions at 20 °C and 65 % relative humidity. Gelatin was purchased from Sigma Aldrich and used as received.

Preparation of wood-gelatin composites:

The wood samples were immersed in an aqueous gelatin solution at 55 °C. The gelatin concentrations used were 30, 60, 90, 100, 120, 180, 250 and 300 mg*ml⁻¹. Subsequently, vacuum was applied for several minutes, followed by reestablishing of atmospheric pressure. This procedure was repeated for multiple cycles.

The wood samples were then removed from the gelatin solution, rinsed with cold water and dried under controlled climate conditions at 20 °C and 65 % relative humidity until further used.

Characterization:

To determine the weight percent gain, the mass of the samples was measured before and after modification after reaching equilibrium (no further change of more than 0.1 % in 24 hours).

For electron microscopy, Raman spectroscopy, and micro X-ray tomography pieces of ca. 0.5 x 0.5 x 0.5 cm³ were cut out from the center of the samples. For electron microscopy and Raman imaging the samples were polished with a rotary microtome (Leica, Germany).

Scanning electron microscopy was executed with a Quanta 200 F microscope at an acceleration voltage of 10 kV. Gelatin layer thicknesses were measured in the SEM images with Image J (US National Institutes of Health, USA).

Micro X-ray tomography was performed with an EasyTom XL Ultra 230-160 device (RX Solutions, France) at an acceleration voltage of 100 kV. Images were collected with a Flat panel detector.

For FTIR spectroscopy, ground samples were used for the measurements. Spectra were acquired on an ALPHA FT-IR spectrometer (Bruker, USA) equipped with an ATR module. They were collected in a spectral range from 4000 cm⁻¹ to 400 cm⁻¹ with a resolution of 2 cm⁻¹. Spectra were averaged over 64 individual scans and baseline-corrected by asymmetric least squares smoothing with the software Origin Pro 2019.

Raman line scans were performed with a confocal Raman microscope (Renishaw InVia, Wotton-under-Edge, England) using a 633 nm laser, a water immersion objective (Nikon, 60X, NA=1.0), a step width of 1 μm , and a 1800 $\text{l}\cdot\text{mm}^{-1}$ grating. Cosmic Ray removal was performed in the software Wire 4.1. (Renishaw) and baseline correction was performed in the software OPUS (Bruker, Germany), using the concave rubberband method.

Contact angles were measured on sessile drops with a DSA 100 device (Krüss GmbH, Germany) and analyzed with the DSA 3 analysis software. For the measurement a drop of deionized water (10 μl) was placed on the sample's microtomed cross section surface. The contact angles on both sides of the drops were measured immediately after the placement of the drop and subsequently every second for the first 30 seconds after the drop placement.

Flow-through experiments:

The flow-through was measured with a customized set-up (Figure S4). The water was pumped by a Masterflex L/S 7523 pump (Cole-Parmer, USA) from a feed reservoir into a sample holder with a constant flow of 50 $\text{ml}\cdot\text{min}^{-1}$ resulting in a maximal trans-membrane pressure of (0.87 ± 0.03) bar. The samples were fixed and sealed inside the holder to only allow flow through the sample. The mass of the permeate was measured with a lab scale. The flux was calculated from the permeate mass increase by time.

Separation of the components:

Wood-gelatin composite samples (thickness 3 mm, 250 $\text{mg}\cdot\text{ml}^{-1}$) were immersed in water at 75 °C for a total of six hours. The water was exchanged after two and four hours, to allow sufficient separation.

Acknowledgements

We would like to thank Thomas Meierhans for the production of the flow-through sample holder and Dr. Selin Vitas for her help with flow-through experiments. Furthermore, Thomas Schnider is acknowledged for cutting the wood samples.

Supporting Information

Additional information as mentioned in the article is available online.

Overview of the sample characterization; X-ray microtomography image of wood gelatin composite; Optical microscopy image of Raman scanning location; time-dependent swelling and water-uptake; scheme of the flow-through set-up; detailed flux values; control experiment for gelatin leaching; videos of x-ray microtomography of unmodified beech wood and of wood-gelatin composite

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TOC graphic:

Synopsis: Modification of wood with gelatin yields an exclusively bio-based composite that can be applied as membrane with tunable flux.