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A versatile strategy for grafting polymers to wood cell walls

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ABSTRACT

The hierarchical structure of wood is composed of a cellulose skeleton of high structural order at various length scales. At the nanoscale and microscale the specific structural features of the cells and cell walls result in a lightweight structure with an anisotropic material profile of excellent mechanical performance. By being able to specifically functionalize wood at the level of cell and cell walls one can insert new properties and inevitably upscale them along the intrinsic hierarchical structure, to a level of large-scale engineering materials applications. For this purpose, however, precise control of the spatial distribution of the modifying substances in the complex wood structure is needed. Here we demonstrate a method to insert methacryl groups into wood cell walls using two different chemistry routes. By using these methacryl groups as the anchor points for grafting, various polymers can be inserted into the wood structure. Strikingly, depending on the methacryl precursor, the spatial distribution of the polymer differs strongly. As a proof of concept we grafted polystyrene as a model compound in the second modification step. In the case of methacryloyl chloride the polymer was located mainly at the interface between the cell lumina and the cell wall covering the inner surface of the cells and being traceable up to 2–3 μm in the cell wall, whereas in the case of methacrylic anhydride the polymer was located inside the whole cell wall. Scanning electron microscopy, Fourier transform infrared spectroscopy and especially Raman spectroscopy were used for an in-depth analysis of the modified wood at the cell wall level.

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1. Introduction

Wood is considered to be one of the oldest building materials. It has been used for thousands of years, because of its remarkable properties such as high mechanical strength in view of its light weight. However, wood also has shortcomings when used as an engineering material. In particular, the water uptake and release by the cell walls under changing relative humidity makes wood prone to fungal degradation and causes swelling and shrinking based on the water adsorption and desorption of cell wall components. The repeated dimensional changes at the microscale and nanoscale eventually lead to cracks and checks within the wood structure, and to the potential failure of wood constructions.

The wood cell wall can be regarded as a hygroscopic biocomposite, consisting of stiff cellulose fibrils embedded in a lignin and hemicelluloses matrix, which can be altered and functionalized via chemical modifications [1–3]. Various protocols to modify wood exist, which differ in their concept (covalent attachment of chemicals to wood cell wall components or bulking), in the utilized chemistry (e.g. esterification and silanization) or in the distribution of the modifying substances in the wood structure (cell wall or lumen). To increase the dimensional stability of wood, one can either reduce the number of hydrophilic OH groups of the wood components through esterification reactions with anhydrides, carboxylic acids or acid chlorides (the new material has less affinity to water molecules) or various substances can be introduced into the wood cell wall in order to fill available free space (bulking) and consequently impede water molecules entering the cell wall [4–13].

It is widely accepted that an efficient wood modification for improving dimensional stability takes place within the wood cell walls, and that the addition of materials into the lumen area likely does not lead to significant changes. Due to the limited accessibility of the cell wall (nanoporosity), most studies use low-molecular-weight molecules for wood cell wall impregnation, with the notable exception of poly(ethylene glycol) oligomers [4,12]. The introduction of polymer chains into the cell wall can be achieved through impregnation of the wood structure with monomers, followed by in situ polymerization. To improve the dimensional stability of wood, it is necessary to introduce a hydrophobic monomer (e.g.

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styrene) into the hydrophilic wood cell wall, with the evident disadvantage that such monomers show little penetration potential. Hence an activation step, which hydrophobizes cell wall components via reaction of the OH functionalities, is essential to improve the penetration of hydrophobic monomers in a second step [14,15]. Furthermore, the polymer chains should be covalently attached to the wood cell wall to achieve a stable modification without leaching of unbound chemicals. One possible approach is to attach a radical initiator to the wood cell wall to initiate in situ polymerization of hydrophobic monomers [16]. Another possibility to anchor polymer chains in the cell wall structure, which is presented here, is to modify hydroxyl groups with polymerizable molecules and to introduce reactive double bonds into the bulk wood in a modular approach. In a first step, methacryl groups were grafted to wood polymers, both using alternatively acid chloride and anhydride functionalities reacting with OH groups. In a second step, the methacryl groups were copolymerized with another monomer, in this case styrene. Based on the modification protocol, the distribution of the methacryl groups and as a consequence the distribution of the introduced second monomer can be varied and controlled depending on the needs for the final product.

2. Materials and methods

2.1. Materials

Methacryloyl chloride, methacrylic anhydride, dry pyridine, acetone, methanol, styrene, 2,2′-azobis(2-methylpropionitrile) (AIBN) and deuterium oxide were obtained from Sigma–Aldrich and used as received.

2.2. Chemical wood modification

2.2.1. Wood samples

Wood cubes of Norway spruce (*Picea abies*) with the dimensions $5 \times 10 \times 10\ mm^3$ (longitudinal × radial × tangential) were prepared. Before treatment the samples were dried at 65 °C for 48 h until a constant mass was obtained. The following abbreviations are used: untreated reference wood (Ref); control samples (Con) treated with pyridine and the same parameters (time and temperature) as the modified samples; methacrylic anhydride or methacryloyl chloride treated wood (respectively Anh and Cl) and in situ polymerized samples (respectively AnhSty and ClSty).

2.2.2. Step 1: methacrylation of wood cubes

Dried wood cubes were placed into a flask under high vacuum for 45 min. In a separate flask a solution of dry pyridine (50 ml) and methacrylic anhydride was prepared. The amount of methacrylic anhydride used was calculated as a two-fold excess (mol) in terms of glucopyranose equivalents (MW = 162 g mol^{-1}). This solution was injected into the evacuated flask with the wood samples, heated to 70 °C and the samples were reacted for 4 h.

For the reaction with the methacryloyl chloride, the following procedure was used. Into the evacuated flask containing the samples, 50 ml of dry pyridine was injected, and in a second step the corresponding amount of methacryloyl chloride was added. The samples were reacted for 75 min. After reaction completion the samples were washed in a methanol: water (1:1 v/v) mixture for 24 h. The washing solution was exchanged five times. The washing procedure was followed by drying the samples at 65 °C until a constant mass was obtained and the wt.% gain was determined.

2.2.3. Step 2: in situ polymerization of styrene

In the second step the methacrylated samples were impregnated with a solution of styrene and AIBN in pyridine. The dried wood samples were placed into a flask and evacuated for 45 min. After the evacuation a solution of styrene in pyridine – 50:50 v/v, containing 1% of AIBN as initiator – was injected to the flask. The solution was heated to 75 °C to polymerize styrene for 20 h. Spruce wood is considered to be one of the wood species which is difficult to impregnate; therefore it was necessary to perform a vacuum impregnation to ensure a homogeneous distribution of the impregnation solution. After completion, the wood cubes were washed with several volumes of acetone for 24 h. Finally, the cubes were dried at 65 °C until a constant mass was obtained.

2.3. Wood characterization

2.3.1. Scanning electron microscopy (SEM)

Smooth surfaces of the wood cubes were prepared using a rotary microtome (Leica Ultracut, Germany). A FEI Quanta 600 probe in the low-vacuum mode (0.53 Torr) and driven at an accelerating voltage of 20 kV equipped with a backscattered electron and secondary electron detector was used.

2.3.2. Thermogravimetric analysis (TGA)

About 10 mg of powdered wood samples was used for the measurement. A TGA Q50 (TA Instruments) with a heating rate of 10 °C min^{-1} (30–800 °C) was used. The measurement was performed under nitrogen atmosphere.

2.3.3. Fourier transform infrared (FTIR) spectroscopy

Powdered wood samples were used for the measurements. Spectra were acquired on a Bruker ALPHA FT-IR equipped with an ATR module. Spectra were baseline-corrected, smoothed in the OPUS software and plotted in OriginPro 8.1.

2.3.4. Raman spectroscopy and vertex component analysis (VCA)

15–20 μm thick cross-sections were prepared using a rotary microtome (Leica Ultracut, Germany). The cross-sections were sealed on a glass slide in wet conditions (deuterium oxide) under a cover slip. For further details on the sample preparation see Ref. [17].

The measurements of the samples were performed with a confocal Raman microscope (Renishaw InVia, Wotton-under-Edge, England) using a 532 nm laser, an oil immersion objective (Nikon, 100×, NA = 1.3, 0.17 mm coverslip corrected) and a 1800 l mm^{-1} grating. As mapping parameters an integration time between 0.15 s and 0.20 s and a step width of 300 nm were used. For the VCA the map data were exported into CytoSpec a commercially available MatLab based software.

2.3.5. Weight percent gain (WPG), volume gain (VG), water uptake (WU) and anti-swelling efficiency (ASE)

The WPG of the modified samples was determined by measuring the mass of the modified samples after each modification step and the VG was determined by measuring the dimensions after the full modification treatment. For the ASE measurements, the initial volumes (oven-dried state) of the modified and reference samples were determined, then the cubes were placed into water with slight stirring until constant volume was obtained. Mass and volume of the wet cubes were measured and then the wood was dried again at 65 °C for 48 h until a constant mass was obtained. Dimensions and weight were determined and the procedure was repeated for one more cycle. For the calculation of the ASE the swelling and shrinkage values of the modified samples were compared to the first swelling values of the untreated reference samples, which gives an indication of the efficiency of the treatment on the dimensional stability. The concept of using various water soaking cycles for the determination of the enhanced dimensional

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