ACS Sustainable Chemistry & Engineering

Letter

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Chemistry and Spectroscopy of Renewable Materials, Part 1: Imaging the Penetration Depth of Covalent Wood Modification

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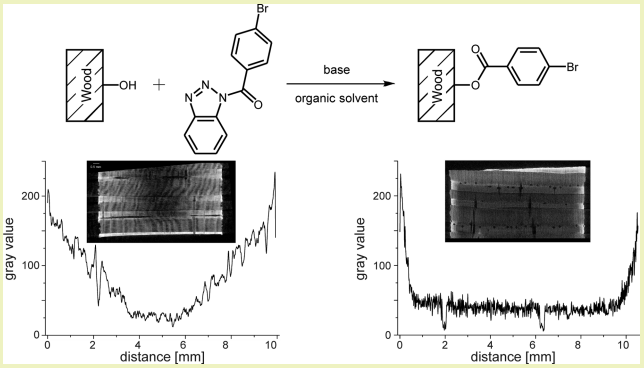
Supporting Information

ABSTRACT: The covalent modification of pine sapwood by benzotriazolyl activated benzoic acids offers broad access to new, durable functional materials. The penetration depth of these substituted benzoic acids remained unknown so far. Two independent proofs were received for the first time by parallel 3D-μCT imaging and attenuated total reflection infrared spectroscopy studies on approximately 10 × 10 × 10 mm wood cubes esterified with activated *p*-bromobenzoic acid. It proved feasible to penetrate pine sapwood anisotropically as deep as 4.5 (with the grain) to 0.75 mm (across the grain), depending on the orientation of the fibers. The results prove the usability of the applied modification procedure.



KEYWORDS: *Wood modification, Covalent fixation, Penetration depth, Anisotropy, Benzoylation, Esterification, Attenuated total reflection IR (ATR-IR), Micro-computed tomography (3D-μCT)*

INTRODUCTION

Current covalent wood modification procedures by benzoylations, as recently published by Kaufmann and co-workers, offer a broad access to new functional materials.[1,2] For example, durable hydrophobization is accessible this way as well as flame protection. Acetylation of wood leads to commercially available materials that were reviewed by Hill.[3] In contrast to unselective modifications of the surface itself as achieved by, e.g., plasma treatments, this method is able to penetrate the desired item also below the surface. This has been proven as a fact by two independent methods: three-dimensional X-ray microtomography (3D-μCT) and attenuated total reflection infrared (ATR-IR) spectroscopy. To the best of our knowledge, this 3D imaging technique has not been applied to esterified wood so far. Nevertheless, after initial medicinal applications, 3D-μCT was applied to composite materials containing wood and ceramics.[4] Recently, drying procedures of wood were also investigated.[5]

Within this work, we present proof of the high efficiency of our recently published wood modification methods.[1,2] Apparently, such modifications are not restricted to the outer wood surface but, in contrast, are effective within a depth of several millimeters. Hence, scratching or other accidental damage does not compromise the properties of the modified wood, a fact that may be essential for further applications, e.g., in furniture industry, inside of a vehicle interior, or other indoor or even outdoor uses. The 3D-μCT imaging was carried out on pine sapwood cubes (*Pinus sylvestris* L.) of approximately 1 × 1 × 1 cm, which prior to this had been modified using a bromo-substituted activated benzoic acid, increasing the density this way, so that high scatter intensities were reached during the 3D-μCT.

MATERIALS AND METHODS

The covalent, and therefore durable, wood modification was achieved by the same methods as stated above,[1,2] but applying prolonged extraction times. All samples were extracted using the reliable solvent-mixture of toluene, acetone, and methanol for a duration of 48 h. The subsequent modification was carried out using (1*H*-benzo[d][1,2,3]-triazol-1-yl)(4-bromophenyl)methanone, an activated derivative of *p*-bromobenzoic acid (see the Supporting Information, Figure S1). The modification procedure of two Scots pine cubes led to two similarly modified items with a weight percentage gain of 33.9% and 33.0%, respectively, which is equivalent to a quantity of 1.85 and 1.80 mmol of covalently bonded organomaterial per gram of wood (QCO).[2]

For the 3D-μCT, no further preparation was necessary. For comparison, an unmodified wood cube was glued to the modified sample. Thus, both cubes were analyzed at the same time to eliminate unintentional side effects. The measurements were carried out with a voltage of 90 kV and a current of 40 μA. The prefilter was made of 0.1 mm copper. The exposure time was set to 1999 ms. The resulting

Received: April 10, 2014
Revised: January 31, 2015
Published: March 9, 2015

DOI: 10.1021/sc5008048
ACS Sustainable Chem. Eng. 2015, 3, 566−568

resolution of each voxel is 7.5 μm. All in all, 1600 projections were measured, to be reconstructed to a complete 3D-dataset afterwards. For analysis the resulting gray values are considered, where a high gray value represents a high density caused by the introduced heavy atom. Additionally, high gray values are equivalent to high brightness. Quantified values were obtained using the software ImageJ (NIH, Maryland, USA).

For the ATR-IR spectroscopy, the first half of a second cube was cut into thin slices of 50 μm each. Every single cut was then analyzed using a Vector 22 FTIR (Bruker, Bremen, Germany) equipped with a Specac Golden-Gate-Diamond-ATR/KRS5 unit. Successively, all single samples were centered on the diamond to obtain the distribution of modification along the longitudinal axis. The resulting spectra were baseline corrected applying the standard method of Bruker OPUS 7.0. For analysis the intensity of three signals was utilized: The carbonyl-band at approximately 1720 cm^{-1}, the signal of the cellulose-backbone at approximately 1030 cm^{-1}, and the aromatic deformation vibration of the newly attached organic compound at approximately 760 cm^{-1}.

RESULTS AND DISCUSSION

The obtained results for the 3D-μCT read as follows: Between the unmodified and the modified sample, there is a huge difference in the gray values. Unmodified wood shows lighter and darker regions, which result from a different density of the material itself (see the Supporting Informations, Figure S2). These differences are based on light early and heavier late wood, respectively.

In contrast to this, a slice image of modified wood (Figure 1, edge; Figure 2, middle) shows extreme differences: The

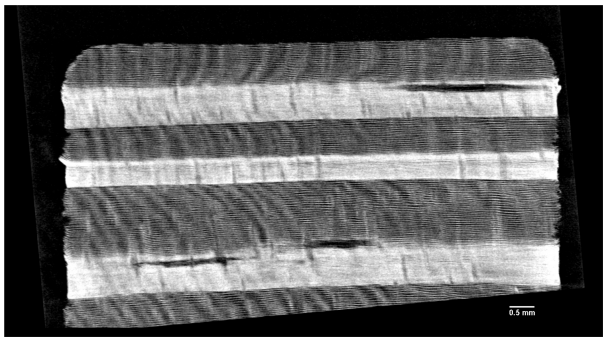


Figure 1. 2D slice image of modified wood at the edge. Viewing direction: radial longitudinal.

complete image has higher gray values, thus reflects a higher density. This higher density is caused by covalent anchoring of bromine-containing organic material onto the wood. Furthermore, there seems to be a distribution along the fiber axis (with

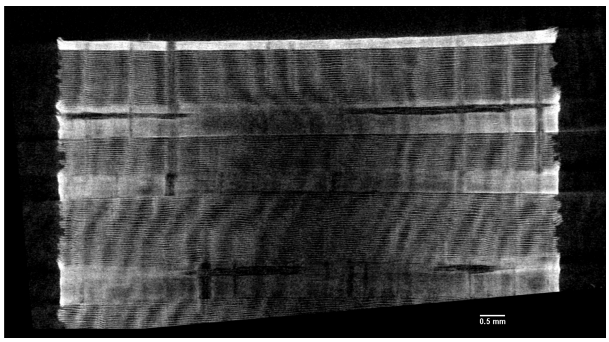


Figure 2. 2D slice image of modified wood at the middle. Viewing direction: radial longitudinal.

the grain) through the modified wood cube due to diffusion and convection processes. Expectedly, the surface is most easily attacked by the reaction mixture and therefore shows higher gray values. However, even the slice image of the middle position shows nicely the effects of both of the distribution processes of the reactants. Although the center itself is already relatively dark, going to the edges, much higher gray values are found.

The plot in Figure 3 depicts the quantified gray values in the middle of the wood sample. The modified cube reveals a

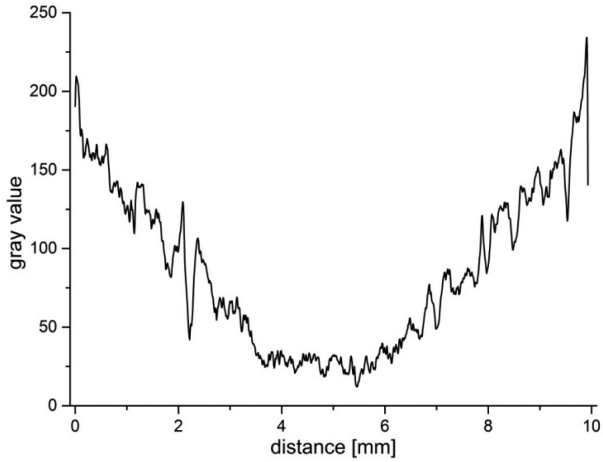


Figure 3. Distribution of gray values for modified wood with high values reflecting brightness in the image and a high degree of modification.

distribution in shape of a goblet with the lowest point at roughly 5 mm from the edge, which is equivalent to the center of the sample.

Flow pathways into the wood are via the lumens of the tracheids in the longitudinal direction with communication between tracheids facilitated by the bordered pits. In the radial direction, flow pathways are primarily associated with the ray cells. With this in mind, the information from Figure 4 is not

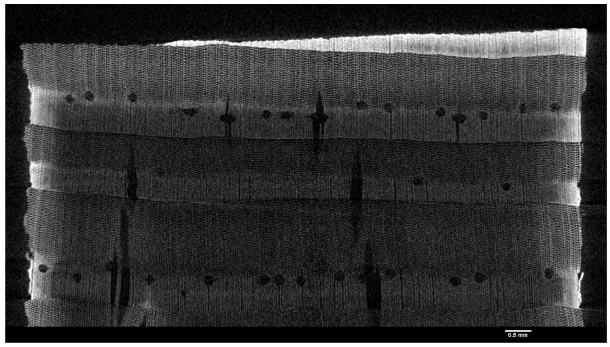


Figure 4. 2D slice image of modified wood at the middle. Viewing direction: transversal.

surprising. It shows a slice image in the middle of the cube but in a direction orthogonal to the one taken for Figure 2. This slice image depicts clearly a high degree of modification at the edges and dramatically decreasing values for the inner part (gray values are given in the Supporting Informations, Figure S4). This leads to the fact that diffusion and convection along

DOI: 10.1021/sc5008048
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the already mentioned channels is essential for the modification process.

All these findings additionally are confirmed by ATR-IR spectroscopy. For every single slice, the spectrum was taken and analyzed for its intensities of the carbonyl, backbone and aromatic deformation vibration signals. Afterward, the gained values for the carbonyl and aromatic deformation bands were plotted in form of their quotient with the backbone. The according results are shown in Figure 5.

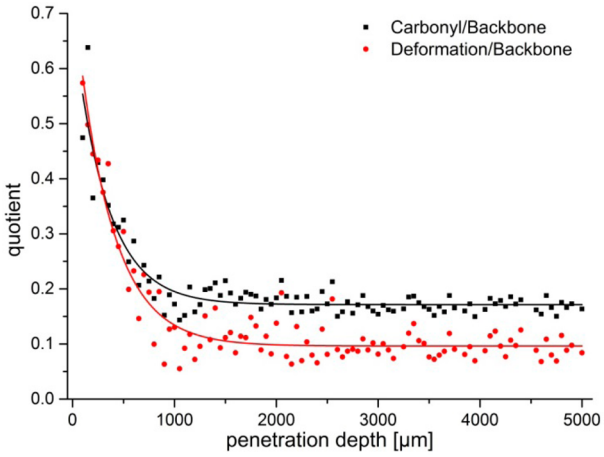

Figure 5. Decay of quotients and exponential fit for ATR-IR bands.

In addition to all notations of single data points, there are exponential fits for each series of these quotients. Starting from the surface the degree of modification drops steadily until about 1 mm penetration depth, but then remains at a considerable level up to 5 mm. The decay indicates again, that the degree of modification is much higher at the outer parts of the cube. As the cube was cut parallel to the projection shown in Figure 2, as expected, the decay shown in Figure 5 is similar to that shown in Figure 4.

CONCLUSION

We were able to prove by two different and independent methods that current covalent wood modification methods are able to penetrate 10 × 10 × 10 mm pine sapwood cubes anisotropically as deep as 4.5 mm. The orientation of the fibers is important for the attainable depth. In the orthogonal direction, a remarkable modification of up to 0.75 mm from the surface was also achieved. The results prove the usability of this way to modify materials, as little scratches or comparable damage will not remove the protection that has been applied by the modification procedure.

ASSOCIATED CONTENT

Supporting Information

Activated *p*-bromobenzoic acid structure and, for comparison, a 2D slice image of unmodified wood beside its gray values plot is available as well as the gray values of Figure 4 and an exemplary ATR-IR spectrum with assigned bands. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We gratefully acknowledge the department for wood biology and wood products of the Georg-August Universität Göttingen for providing the wood samples and support for the thin slices.

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DOI: 10.1021/sc5008048
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