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Section 4 **Processes and properties**

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Studying amount, location and state of water in modified wood at moisture levels relevant for fungal degradation

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ABSTRACT

Water is an essential parameter for fungal degradation of wood, but degradation primarily occurs at high moisture levels at water potential in the range of -4 to -0.1 MPa, which corresponds to 97-99.9% relative humidity. At these moisture levels, water is present in the wood structure both in and outside of cell walls. The majority of previous studies on the interaction between wood and water for untreated as well as modified wood has, however, focused on the moisture range 0-95% relative humidity and mainly on water in cell walls. In this paper, we give examples of how precise conditioning of specimens using the pressure plate technique can be combined with other experimental techniques in order to get information on interactions between wood and water at humidity levels relevant for fungal degradation. We show examples of how pressure plate conditioning can be combined with Differential Scanning Calorimetry (DSC) and Low Field Magnetic Resonance (LFNMR) to get information not only about amount of water, but also about location and state of water in untreated and modified wood. Further use of such combination of techniques has potential to give valuable pieces of information on the role of water in degradation processes for untreated as well as modified wood.

Keywords: experimental methods, modified wood, moisture, pressure plate, sorption, water, water potential

1. INTRODUCTION

Water is an essential parameter for fungal degradation of wood. In wood, water is taken up both in cell walls and as capillary water in macro voids such as cell lumina and pit chambers. Inside cell walls, water interacts with hydroxyl groups of the chemical constituents and affects physical properties such as swelling/shrinkage and strength. Capillary water in wood macro voids is only present to a significant extent at high humidity levels when capillary condensation occurs in the macro voids, or, when wood is exposed to liquid water, e.g. in rain exposed structures. The minimum water potential that allows activity of wood degrading fungi is in the range of -4 to -0.1 MPa (Griffin 1977; Boddy 1983; Griffith and Boddy 1991; Schmidt 2006), which corresponds to 97-99.9% relative humidity. The relation between wood and water has been widely studied, but historically, a lot of focus has been on amount of water, i.e. how much water the wood contains and most studies concern relative humidity levels up to 95% RH, i.e. a moisture range where fungal degradation generally does not occur.

Wood modification with acetic anhydride, acetylation, increases the resistance to fungal degradation (Alfredsen *et al.* 2016). Acetylation lowers the amount of water present in cell walls (Himmel and Mai 2015) since it replaces water-attracting hydroxyl groups with acetyl-groups that have lower affinity to water and takes up space otherwise available for water. The lowered cell wall moisture content has been suggested as a possible reason to the enhanced durability since a low cell wall moisture content could hinder the transport of substances necessary for the fungi (Zelinka *et al.* 2016). However, wood-degrading fungi also need capillary water to be present (Zabel and Morell 1992; Schmidt 2006) and interestingly acetylation changes also the amount and state of this water (Thygesen and Elder 2008; Thygesen *et al.* 2010; Beck *et al.* 2017). The moisture uptake of acetylated wood at high humidity levels (the over-hygroscopic range) is however much less explored than at lower levels up to about 95% relative humidity (RH) (the hygroscopic range), most probably because experimental studies at such high moisture levels requires special laboratory equipment. In the hygroscopic range, specimens are commonly equilibrated to different RH levels using saturated salt solutions. However, this is not possible in the over-hygroscopic range since that requires impossibly accurate and precise temperature stability to avoid condensation. Instead, a technique called pressure plate (e.g. Defo *et al.* 1999; Fredriksson and Thybring 2019) is used. This conditioning technique is beneficial as it provides a high resolution for RH levels close to 100%. For example, a pressure of 1 bar corresponds to 99.93% relative humidity (RH), and a pressure of 2 bar corresponds to an RH of 99.85%.

In this paper, we give examples of how pressure plate conditioning can be combined with other measurement techniques in order to get information not only about amount of water, but also about location and state of water in untreated and modified wood.

2. MEASURING AMOUNT OF CELL WALL WATER AT HIGH HUMIDITY LEVELS

At high humidity levels, water is present both within and outside of cell walls. It is therefore interesting to determine not only total moisture content but also how this water is partitioned between cell walls and capillary water in macro voids. Since water outside cell walls freezes when exposed to sub-zero temperatures and water in cell walls does not, it is possible to separate water inside and outside of cell walls using Differential Scanning Calorimetry (DSC). This has been done multiple times for water-saturated wood (e.g. (Simpson and Barton 1991; Digaitis *et al.* 2017)), but recently Fredriksson and Thybring (2019) combined DSC (Q2000 DSC, TA Instruments, Eschborn, Germany) with conditioning using the pressure plate technique. In that study, specimens were conditioned to several high moisture states in both absorption and desorption using a novel setup based on the pressure plate technique. After conditioning, DSC measurements were performed to separate the total moisture content into cell wall water and capillary water. This enabled determination of cell wall moisture contents in both desorption and absorption in the moisture range where wood degrading fungi are active (Fig. 1). In the study by Fredriksson and Thybring (2019), only untreated wood was used, but it is possible to use the methodology for modified wood as well. This would result in more detailed information of cell wall moisture content in modified wood at moisture levels relevant for degradation.

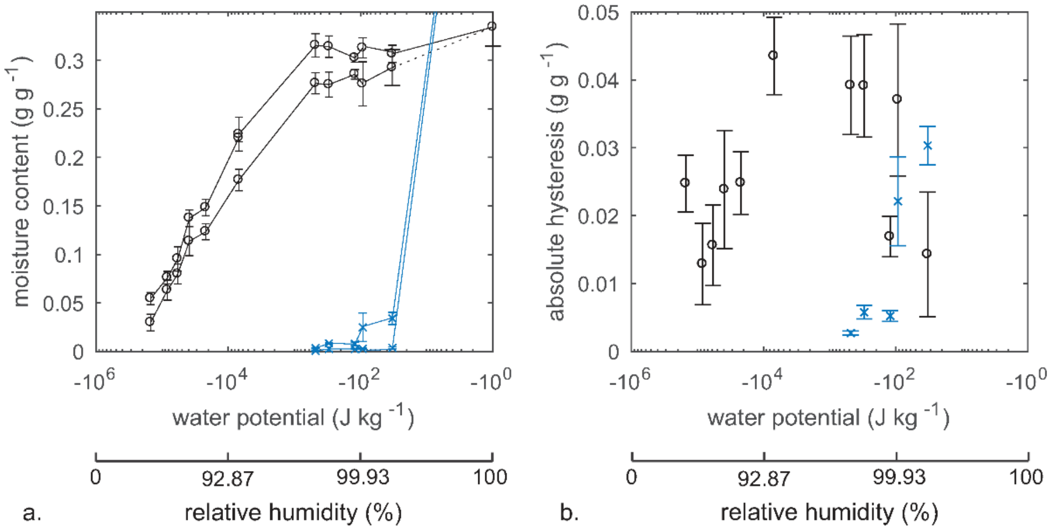

Figure 1: a. Sorption isotherms for water in cell walls (black) and water outside of cell walls (blue). The upper curve is the desorption isotherm and the lower curve is the absorption isotherm in both cases.
b. Sorption hysteresis for cell wall water (black) and water outside of cell walls (blue) determined as absolute difference in moisture content between desorption and absorption. Figure from Fredriksson and Thybring (2019)

3. LOCATION AND STATE OF CAPILLARY WATER AT HIGH HUMIDITY LEVELS

Low-field Nuclear Magnetic Resonance relaxometry (LFNMR) can be used to study state and location of water (Thygesen and Elder 2008; Beck *et al.* 2017). A change in the spin-spin relaxation time, T_2, indicates a change in wood-water interactions, which can be due to either change in physical environment (surface-to-volume ratio of the pores) or chemical environment (surface chemistry inside pores or solutes in the water). Since T_2 is related to the surface-to-volume ratio of pores, the amount of water in differently sized voids can therefore be evaluated by the area below the peaks obtained in the T_2 distributions (Fredriksson and Thygesen 2017). However, modifications such as acetylation, changes the chemical environment and increased degree of acetylation increases the T_2 (Thygesen and Elder 2008; Beck *et al.* 2017). An example of this is shown in Fig. 2 where LFNMR-measurements (mq20-Minispec, Bruker, Billerica, MA, USA) initially were performed on water saturated untreated specimens of spruce (*Picea abies* (L.) Karst.) and oak (*Quercus robur* L.). After the LFNMR measurements, the same specimens were acetylated which gave weight percent gains (WPG) of 23% (std.dev. 0.2) and 19.5% (std.dev. 0.3) for spruce and oak respectively. As seen in the Fig. 2, the T_2 of all peaks then increased due to the change in chemical environment.

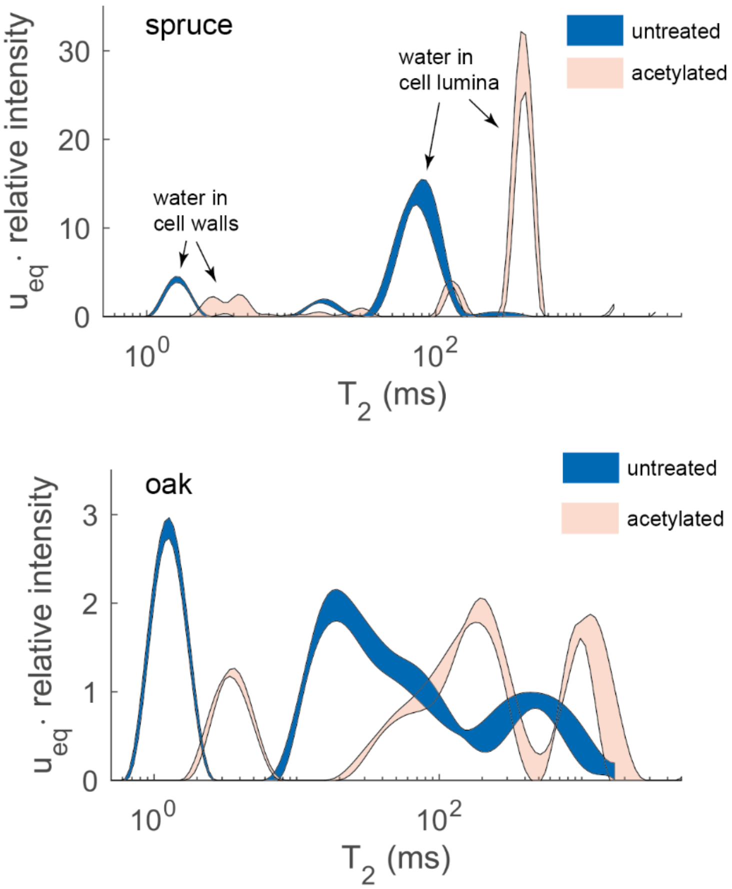

Figure 2: Results from LFNMR measurements for spruce and oak. The range shows the average value plus/minus the standard deviation. Blue curves are for untreated water saturated specimens and pink curves for acetylated water saturated specimens.

The results shown in Fig. 2 were acquired from water-saturated specimens, but the LFNMR-technique can also be used on non-saturated specimens. However, drying wet specimens in an undefined environment induces moisture gradients and if the moisture content is different in different parts of the specimen it may be challenging to interpret the data. Therefore, water-saturated spruce and oak specimens were conditioned in a pressure plate cell at 1 bar which corresponds to an RH of 99.93%. After an equilibration period of 13 weeks, the specimens were transferred to glass tubes, sealed and then measured with the LFNMR equipment. The results are seen in Fig. 3 which shows that the peak representing capillary water in cell lumina has decreased. This is a result of emptying of some of the cell lumina. In the case of spruce, it is most likely the earlywood lumina that were emptied. This is because the size of the bordered pit openings and the cell lumina in itself is larger in earlywood than in latewood. For oak, the peak with the longest T_2 disappeared indicating that the largest cell lumina (vessels) were emptied by conditioning at 99.93% RH.

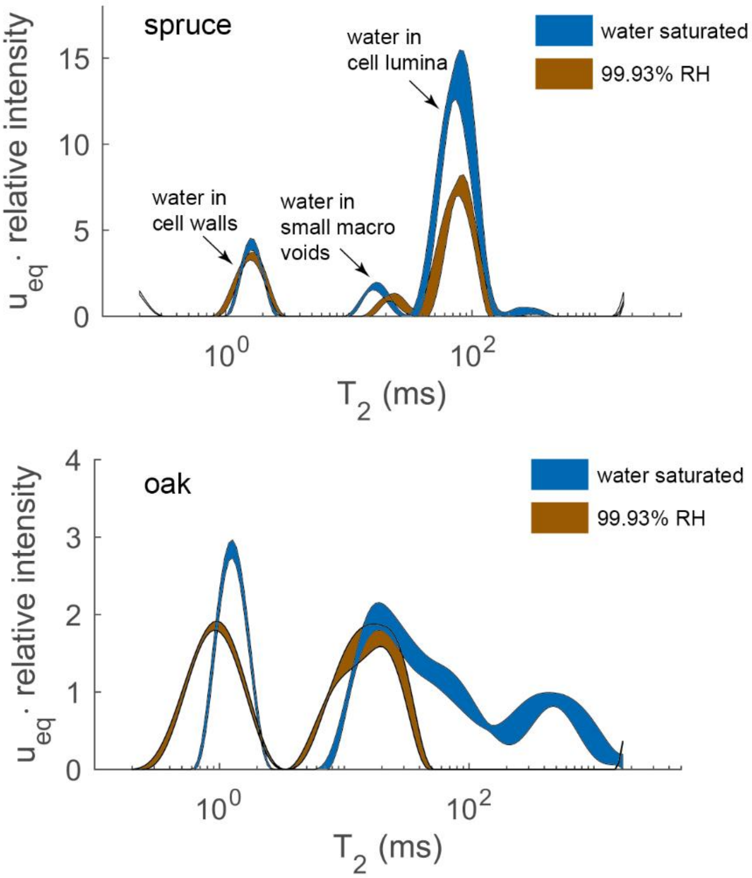

Figure 3: Results from LFNMR measurements for spruce and oak. The range shows the average value plus/minus the standard deviation. Blue curves are for water saturated specimens and brown curves for specimens conditioned at 1 bar (99.93% RH) by the pressure plate technique.

To further explore how LFNMR can be used on modified wood at different high humidity levels, acetylated spruce specimens (WPG 12.8%) were conditioned at seven different RH levels in both absorption and desorption using the pressure plate technique. The results are shown in Fig. 4, where the continuous T_2 distributions show the distribution of water between different locations in the wood structure at the different RH levels. In absorption, water was not present in cell lumina in the RH range between 99.65 and 99.98%. In desorption, on the other hand, water was present down to 99.71% RH. This difference is caused by a difference in water uptake mechanisms between absorption and desorption at these high moisture levels. In absorption, water uptake in macro voids occurs by capillary condensation at an RH that depends on pore size, pore geometry and the contact angle between the water and the solid material (Gregg and Sing 1967). Due to the large dimensions of the cell lumina, RH levels extremely close to 100% is needed for this to happen. For example, assuming cylindrical geometry and contact angle 0 °, capillary condensation in a pore with radius 10 µm occurs at 99.989% RH (Fredriksson 2019). In desorption, however, the RH at which cell lumina is emptied depends on the size of the openings; this is generally referred to as the ink-bottle effect (Gregg and Sing 1967). The emptying of lumina therefore occurs at a lower RH, i.e. the RH that corresponds to the size of the pit openings.

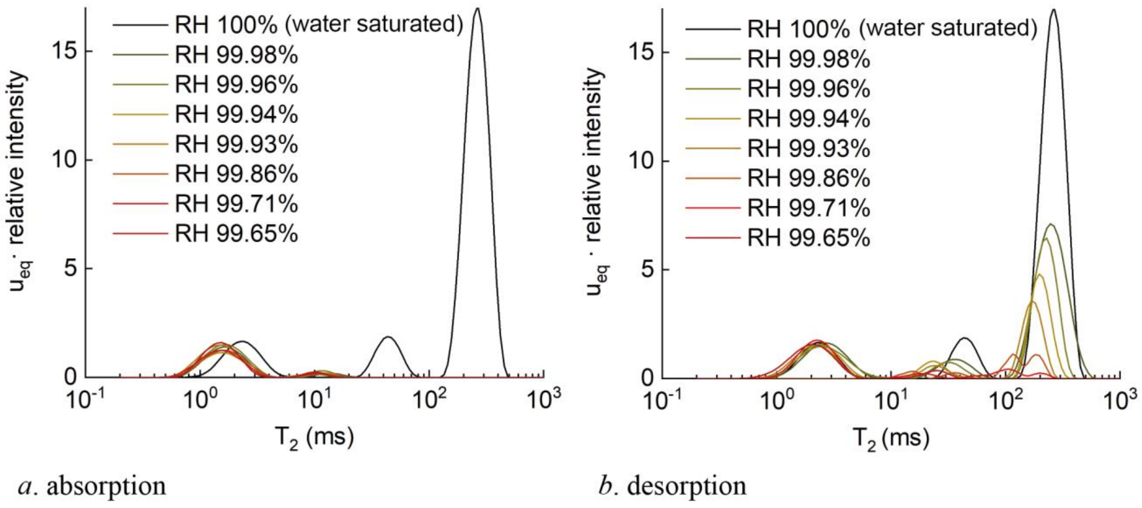

Figure 4: Results from LFNMR measurements for acetylated spruce (WPG 12.8%) in water saturated state and conditioned to 7 different RH levels in absorption (*a*) and desorption (*b*) by the pressure plate technique. Each curve is the average curve for three replicates.

4. CONCLUSION

By combing different experimental methods it is possible to study amount, location and state of water in untreated and modified wood at moisture levels relevant for fungal degradation.
This can give valuable pieces of information on the role of water in degradation processes.

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