

Water sorption in wood and modified wood at high values of relative humidity. Part I: Results for untreated, acetylated, and furfurylated Norway spruce

Lisbeth G. Thygesen^{1,*}, Emil Tang Englund^{2,3} and Preben Hoffmeyer³

¹ Forest and Landscape, University of Copenhagen, Frederiksberg C, Denmark

² Wood and Textile, Danish Technological Institute, Taastrup, Denmark

³ Department of Civil Engineering, Technical University of Denmark, Lyngby, Denmark

*Corresponding author.

Forest and Landscape, University of Copenhagen, Rolighedsvej 23, DK-1958 Frederiksberg C, Denmark
E-mail: lgt@life.ku.dk

Abstract

Desorption isotherms at 20°C for untreated, acetylated, and furfurylated Norway spruce [*Picea abies* (L.) Karst.] sapwood were established in the 91.9–99.9% relative humidity (RH) range. Three methods were employed to secure various constant RH levels: saturated salt solutions, climate chambers, and the pressure plate technique. The curve form for the untreated samples did not show an upward bend, except perhaps above 99.5% RH, indicating that – contrary to what has hitherto been assumed – capillary condensation does not play a significant role for water sorption in wood below fiber saturation. Three additional results corroborate this conclusion: (1) calculation of the theoretical contribution of capillary condensation to the moisture content (MC) in wood based on idealized microstructural geometries by means of the Kelvin and Laplace equations resulted in very small contributions to the equilibrium moisture content (EMC), i.e., below 0.35% moisture at 99.9% RH. (2) The ratio between the EMC of acetylated and untreated samples did not show an increasing trend for increasing RH, as would have been the case if capillary condensation had taken place in both untreated and acetylated wood. (3) Low field time domain nuclear magnetic resonance results showed that only the relaxation curves from the furfurylated samples were affected systematically by freezing, indicating that neither untreated nor acetylated wood contained significant amounts of capillary condensed water.

Keywords: acetylation; capillary condensation; furfurylation; isotherm; sorption; wood-water relations.

Introduction

Moisture in wood has been studied for decades. Several explanations have been suggested regarding the way water

molecules are bound in the wood structure as a function of the relative humidity (RH). One such explanation often cited relates the uppermost part of the sorption isotherm to capillary condensation in voids in the material (Sheppard 1933; Barkas 1937; Babbitt 1943; Stamm 1950; Spalt 1958; Kollmann 1962; Simpson 1973). However, the question of capillary condensation at high levels of RH has not yet been resolved. The present study employs three techniques (saturated salt solutions, climate chambers, and the pressure plate technique) to examine the nature of moisture in wood in the RH range from 91.9% to 99.9%. Furthermore, two different types of chemically modified woods are included in the experiments as a tool to highlight the sorption behavior of untreated wood.

Void radii and capillary condensation

In the following, cavities, pores, voids, etc., in wood are categorized and termed according to their dimensions (Griffin 1977). This system complies better with wood anatomy than the IUPAC definition of pore size classes (Sing et al. 1985; Rouquerol et al. 1994). *Macrovoids* comprise the lumina of cells with radii from approximately 5 μm to 200 μm or greater. *Microvoids* include the pointed ends of lumens, pit apertures, pit-membrane voids, and other small voids with radii in the range from 5 nm to 5 μm . *Nanovoids* are found in the cell wall and range in size from 5 nm down to the level of single water molecules bound to hydrophilic sites of the wood polymer, at which level the concept of pore radii becomes meaningless. It is a generally accepted assumption that the dry cell wall is essentially non-porous (Griffin 1977; Fahlén and Salmén 2005; Salmén and Fahlén 2006) and that nanovoids emerge as a result of the presence of water. Measurements on different wood species in either green or saturated condition show a maximum nanovoid size of 1.8 nm for green spruce (Stone and Scallan 1968), 0.9–1.0 nm for green Sitka spruce (Tarkow et al. 1966), 0.8 nm for saturated sweetgum (Flournoy et al. 1991), and 2 nm for saturated Corsican pine (Hill et al. 2005).

The Kelvin equation relates the relative humidity to the void radius that leads to capillary condensation within voids of these dimensions. Corresponding values of RH and void radius are given in Table 1. It has long been debated in what range the Kelvin equation is valid. Skaar (1988) argued that below 80% RH the concept of capillary condensation is questionable, as at this RH the corresponding pore radius of 4.9 nm was only approximately 15 times the diameter of a water molecule (0.3 nm). Measurements of menisci in mica capillaries of 5 nm diameters confirm that the Kelvin equation is valid down to approximately 80% RH (Kohonen and

Table 1 Values of relative humidity (RH), capillary radius, and corresponding matrix component, ψ_m , of water potential at 20°C.

RH (%)	Water potential (MPa)	Capillary radius (μm)	Void type
99.999	-0.00136	108	Macro
99.99	-0.0136	10.8	
99.98	-0.0271	5.42	
99.9	-0.136	1.08	Micro
99.8	-0.271	0.542	
99.5	-0.679	0.216	
99	-1.36	0.108	
98	-2.74	0.0537	
97	-4.13	0.0357	
95	-6.95	0.0211	Nano
90	-14.3	0.0103	
85	-21.9	0.0067	
80	-30.2	0.00487	
75	-69.2	0.00378	

Christenson 2000). Other studies (Lastoskie et al. 1993; Rouquerol et al. 1999) have shown that the Kelvin equation cannot be extended below a void radius of 3.75 nm and a relative water vapor pressure of 75%. Below this pressure, the capillary condensation is controlled by the specific interaction between sorption sites and the condensed vapor and not by the Kelvin equation (Evans 1990). However, capillary condensation can still take place below 75% RH. For instance, Branton et al. (1995) have studied the capillary condensation in the porous silicate material MCM-41, which has a specific pore size of narrow distribution. They found that capillary condensation occurs in a narrow range of RH of approximately 55%. At such low RH, however, the mechanisms controlling the condensation cannot be described by the Kelvin equation. Consequently, the values of pore radii are presented in Table 1 as calculated from the Kelvin equation down to 75% RH.

Table 1 also lists water potentials as given by the Young-Laplace equation. This equation is very useful in pore size studies if the pressure plate technique (PPT) is used, also known as the suction technique, which is a method for studying desorption isotherms and pore size distributions at very high levels of RH. The pressure-EMC (equilibrium moisture content) relation can be transformed into a desorption isotherm for high values of RH and subsequently used for pore size assessment (Tremblay et al. 1996; Defo et al. 1999) by combining the Kelvin and the Laplace equations. However, caution should be exercised when interpreting such assessments because the method is strictly valid only for pores in a rigid material. However, the number and sizes of pores in wood are functions of RH. A drop in RH, therefore, results in pores losing some of their water while at the same time collapsing to the size in equilibrium with the new RH (Robertson 1965; Alinec 2002).

Water in wood

The general concept of water in wood used here is largely based on Berthold et al. (1996) and Salmén (1997). According to these authors, water is held as non-freezing bound water, freezing bound water, and free water. This classification is a refinement of that used by Stamm (1950), who did not distinguish between the two bound water types. *Non-freezing bound water* is water specifically bound to hydrophilic sites (hydroxyl groups) of the three main wood polymers, mainly hemicelluloses. In uncharged carbohydrates, each polar hydroxyl group has on average approximately one water molecule adsorbed at 92% RH, increasing to approximately 1.3 at 98% RH (Berthold et al. 1994). Non-freezing bound water is found in nanovoids and as wall lining of macrovoids and microvoids. *Freezing bound water* is the more loosely bound water in the larger water clusters. Thus, freezing bound water is only indirectly bound to the hydrophilic sites of the wood polymers. Freezing bound water is found at high RH in nanovoids and as wall lining of macrovoids and microvoids. This type of water exhibits freezing point lowering. Berthold et al. (1994) did not find by differential scanning calorimetry any freezing bound water down to -90°C in uncharged carbohydrates for EMCs up to 98% RH. Freezing bound water was only found in carbohydrates containing charged groups. *Free water* in wood is held in microvoids and macrovoids. The term *free* only signifies that water molecules are not bound to specific sorption sites; it is still bound by capillary forces and has a negative water potential. Stamm (1950) refers to this type of water in wood as capillary water. This type of water exhibits little freezing point lowering.

Water in modified wood

One of the purposes of the present work was to study moisture in acetylated wood and in furfurylated wood at high RH. Both treatments are chemical modifications aimed at reducing the moisture uptake thus enhancing dimensional stability and decay resistance.

Regarding acetylation, each acetyl group is known to be linked covalently to a hydroxyl sorption site in the cell wall (Papadopoulos and Hill 2003). Acetylation therefore should not be capable of filling cavities significantly larger than the acetyl group themselves, but only form a layer on part of the walls of the cavity. The size of an acetyl group is influenced by its nearby environment (Kwon et al. 2007). However, computer simulations of acetylated galactopyranose by Thibodeaux et al. (2002) can give an idea of the size. In these simulations the bond lengths of the O-C and C-CH₃ bonds was found to be 0.135 nm and 0.149 nm, respectively (Thibodeaux et al. 2002). If the C-H bond length is estimated to 0.109 nm (Demaison and Wlodarczak 1994) and the van der Waals radius of the hydrogen to 0.120 nm (Bondi 1964), the maximum distance from the oxygen of the wooden substrate to the end of the acetyl group is approximately 0.52 nm (assuming a linear O-C-C-H structure). This should be seen in relation to the size of the initial hydroxyl group where an

O-H bond length of 0.0946 nm (Szalay et al. 2002) results in a distance from the oxygen to the end of approximately 0.22 nm. Thus, based on estimates of bond lengths, the acetyl groups add approximately 0.3 nm at each sorption site where it bonds. Capillary sorption in pores with a radius significantly larger than the dimension of the acetyl group should therefore remain unaffected by acetylation, provided that there is no change of contact angle. There are, however, indications that the contact angle in macrovoids is affected by acetylation (Thygesen and Elder 2008). A theoretical quantification of the influence of contact angle on capillary moisture uptake is found in Part 2 of this article. For RH values where EMC is governed by sorption directly at hydroxyl sorption sites, an almost constant ratio between the EMCs of acetylated and untreated wood would be expected, largely reflecting the degree to which the acetyl group is blocking access of water molecules to hydroxyl sorption sites. An EMC ratio increment in the range of high RH could indicate contribution from capillary sorption (Strømdahl 2000), which is supposed to be unaffected by acetylation. This reasoning is valid only if it can be assumed that acetylation does not create new voids of a size relevant for capillary sorption at high RH. Microvoids and macrovoids caused by acetylation have not been reported in the literature. Based on these findings, acetylated wood samples were included here as a type of modified wood where direct blocking of hydroxyl groups through the formation of covalent bonds presumably played a more important role for the sorption properties than bulking of voids in the 91.9–99.9% RH range.

It is presently not exactly known how furfurylation reduces moisture uptake. It was recently shown (Nordstierna et al. 2008) that furfuryl alcohol can form covalent bonds to lignin model compounds. However, such a reaction has not been shown for wood lignin *in situ*. Furthermore, bonds to lignin will not directly block sorption sites in the carbohydrate part of the wood cell wall material, i.e., the part of the wood where most of the primary sorption takes place. Other recent studies indicate that a furfuryl alcohol based polymer (FAP) is formed within the wood, a polymer which is bulking the cell wall (Venås 2008; Thygesen et al. 2010; Thygesen and Elder 2009). Furfurylated wood was included here as a type of modification where bulking presumably played a more important role for the sorption properties than direct blocking of hydroxyl groups through the formation of covalent bonds.

Materials and methods

Wood samples

Two differently shaped sapwood samples were included: cylinders and cuboids. Cylinder shaped samples with a diameter of 14 mm were drilled from the sapwood of 10 mm thick discs taken from a stem of Norway spruce [*Picea abies* (L.) Karst.], whereas cuboids measuring 1×40×40 mm were cut from the sapwood of other discs from the same stem. Processing of the stem took place within a few days after harvest, and care was taken throughout to prevent samples from drying out. After processing, the samples were stored in sealed plastic bags with an excess of demineralized water. All samples

were then subjected to neutron radiation (1×15 kGy) to prevent biological degradation during storage (mould fungi). As a further precaution, samples were stored at +5°C.

Three types of wood samples were produced:

- *Untreated samples (denoted U)* were dried at 103°C and then vacuum saturated with demineralized water containing sodium azide (NaN_3 , 200 mg l^{-1}). The samples were saturated in the water for 2–3 h at 2.6–3.0 kPa followed by 24 h at atmospheric pressure.
- *Acetylated samples (denoted A)* were treated in a lab-scale set-up adapted from Rowell (1986). The samples were dried at 103°C and then subjected to vacuum drying for 18 h, after which enough acetic anhydride was added to cover all samples. After 1 h, the pressure was equilibrated, and the samples were boiled ($\sim 140^\circ\text{C}$) in acetic anhydride for 4 h. Finally, the samples were dried at 103°C for approximately 24 h. The average weight percent gain (WPG) was 20%. After acetylation the samples were vacuum saturated in the same way as the untreated samples (type U).
- *Furfurylated samples (denoted F)* were treated in a lab-scale set-up. Samples were pre-dried at 103°C for 16 h and impregnated in an autoclave (full vacuum for 30 min followed by a pressure of 1.2 MPa for 120 min). Excess liquid was wiped off, and the solvent was partly evaporated in an oven using a temperature ramp from 20°C to 40°C during 4 h. Subsequently, the samples were wrapped in aluminum foil and cured for 16 h at 103°C. The foil was removed, and the samples were dried for 7 h at 103°C to evaporate condensed water and unreacted monomer. The impregnation fluid consisted of furfuryl alcohol (55 wt-%), ethanol (39 wt-%), citric acid (catalyst, 2 wt-%), and deionized water (4 wt-%). The average WPG was 63%, indicating that the impregnation was successful even though the samples were made from spruce. This is most likely as a result of the small sample dimensions used. After furfurylation, the samples were vacuum saturated in the same way as the untreated samples (type U).

Relative humidity levels and equilibrium moisture contents

Relative humidity levels (21 totally) were established at 20°C by three methods: saturated salt solutions, climate chambers, or the PPT. All EMCs were reached from higher MCs, i.e., through desorption. The criterion employed for determining whether EMC had been reached was that the sample weight did not vary more than 0.5% over 2 weeks, or, for the PPT method, that there had been no outflow of water for 2 weeks.

Saturated salt solutions in desiccators were employed to reach the following RH levels: (1) 91.9% RH (BaCl_2), according to a linear regression between temperature and RH based on values from Apelblat (1992), (2) 94.1%, and (3) 97.7% RHs obtained with saturated KNO_3 and K_2SO_4 solutions, respectively, according to Hansen and Jensen (2002). The desiccators were placed in a 20°C water bath in an isolated chamber. Magnetic stirring of the solution was used throughout the experiment to ensure a homogeneous RH distribution within the desiccators. The samples were taken out and weighed once every 1–2 weeks. The time to equilibrium was approximately 5 months. Both cuboids and cylindrical samples were conditioned.

Other samples were conditioned in climate chambers at the Department of Civil Engineering, Technical University of Denmark (Strømdahl 2000). This system allows weighing of the samples within the chambers. Two chambers were available in parallel, and

the RH levels were 98.0%, 96.0%, and 94.7%, respectively, 97.6%, 96.2%, and 94.9%. Samples were weighed once or twice a week, and the time to equilibrium was 2–5 months for each RH level. The total duration of the experiment was approximately 1 year. Both cuboids and cylindrical samples were treated as described.

The principle of the PPT method is to expose water saturated samples to a pressure of up to 10 MPa while they are in hydraulic contact with atmospheric pressure through a ceramic disc or a cellulose membrane with fine pores. Water will then flow out of the samples until they are in equilibrium with the applied pressure. By combining the Kelvin and the Laplace equations the RH that corresponds to the applied pressure can be calculated, assuming that the sample is stiff and porous and partially water filled. For a given pressure it is then hypothesized that pores with a diameter larger than a limit value corresponding to the applied pressure are emptied of liquid water. A description of the method can be found in Penner (1963) and Cloutier and Fortin (1991).

Two different systems placed in two different laboratories were employed, one at the Technical University of Denmark (DTU), and one at Lund University (LU), Sweden. Both systems were based on equipment from Soilmoisture (Santa Barbara, CA, USA) and three different extractors intended for different pressure ranges were employed at both laboratories (0–0.5, 0–1.5, and 0–10 MPa). However, the 0–10 MPa unit of the Danish system had been slightly modified as described in Thygesen and Hansen (2007). Table 2 gives an overview of the PPT experiments carried out. All three types (U, A, and F) were always included in each run, i.e., situated in the same extractor and subjected to the exact same pressure. The outflow of water from the extractors was checked 2–5 times a week, and the time to equilibrium was in each case 2–3 months. Only cylindrical samples were used for the PPT experiments, and they were always placed with one of the two flat faces facing the disk, i.e., water was made to move along the grain, which should ensure the shortest possible time to equilibrium (Cloutier et al. 1995).

Following all types of conditioning experiments, samples were dried at 103°C and weighed. Mean MCs were calculated for each sample type based on the total dry weight of all samples of the same type subjected to the same RH level within the same experiment. It has recently been suggested to calculate MCs of modified wood samples based on their dry weight before modification, thus excluding the weight of the added substances (Hill 2008; Venås 2008). However, in this study, only average WPG values for each

modification type (acetylation and furfurylation) were known. We consequently report for each sample the MC results based on an estimated dry weight of an unmodified sample. If the results were reported on the basis of the dry weight of the modified sample, the WPG variation between samples would still be included in the results. Thus, no additional uncertainty is introduced by estimating the dry weight of the unmodified samples.

Low field time domain nuclear magnetic resonance (LF TD NMR)

A subset of the samples was subjected to LF TD NMR at two temperatures. For each measurement four cylindrical samples of the same type (U, A, or F) conditioned to the same RH level were measured together to achieve the recommended tube filling for each NMR measurement. For each sample type, 36 such samples were prepared. Instrument: 23 MHz ¹H NMR Maran (from Resonance Instruments, now part of Oxford Instruments, UK) set to a temperature of +20°C. The free induction decay was recorded by a recycle delay of 2 s and 32 acquisitions. In total, 8000 data points with a spacing of 0.5 ms were recorded. Just before measurement, the samples were weighed to allow MC determination.

After measurements the samples were put in a freezer at -18°C for at least 24 h. Then they were placed in a cooling bath at -20°C for at least 1 h. The temperature just below the position of the tube inside the NMR instrument was set to -20°C by a custom-built cooling system based on evaporation of liquid nitrogen. The samples were then remeasured at this temperature before they were dried at 103°C to constant weight to determine their MC during the +20°C measurement.

Results and discussion

Sorption isotherms

The desorption data are presented in Figure 1. As can be seen, the experiment was designed with overlaps between the three methods. These overlaps show that the EMCs found for the same sample type and at the same RH level, but by different methods, are not systematically different. In other words, there are no discontinuities between methods; a feature that lends the isotherms high credibility.

As seen from Figure 1, the EMCs of the untreated samples at the high end of the RH scale (above 98%) are around 40%, i.e., well above the rule-of-thumb value of approximately 30% often assumed to be the fiber saturation point (FSP) of European softwood. However, as pointed out already by Stamm (1971), the FSP depends on the method applied, and our results for RH >98% obtained by the PPT method are in fact well in line with earlier PPT results regarding the FSP of untreated softwood (Stone and Scallan 1967; Stamm 1971; Griffin 1977; Hill et al. 2005).

Sorption isotherms in the 96–99% RH range are often drawn with an upward bend (Spalt 1958; Kollmann 1962; Simpson 1973). Typically, it is assumed that at very high humidity levels, capillary sorption in microvoids in the cell wall structure is of crucial importance to the MC. However, such an upward bend is not seen in our data for untreated samples, except perhaps a weak tendency above approxi-

Table 2 Overview of the pressure plate technique (PPT) experiments.

Laboratory ^a	Extractor, max pressure (MPa)	Pressure (MPa)	RH (%)
LU	10	5.60	95.9
LU	10	4.05	97.0
DTU	10	2.73	98.0
DTU	10	1.36	99.0
LU	1.5	1.36	99.0
DTU	1.5	0.66	99.5
DTU	0.5	0.38	99.7
DTU	0.5	0.27	99.8
LU	0.5	0.28	99.8
DTU	0.5	0.14	99.9

^aLund University (LU), Technical University of Denmark (DTU).

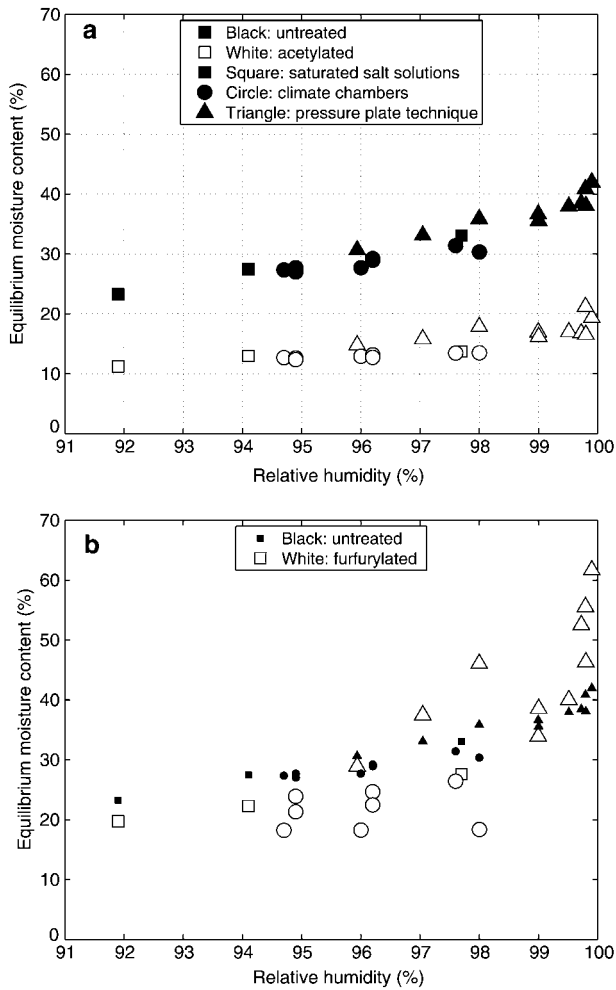


Figure 1 Desorption data for untreated, acetylated, and furfurylated samples. For each data point it is also indicated which of the three different methods mentioned in the legend that was employed for establishing a constant relative humidity level.

mately 99.5% RH. The highest RH value (99.9%) obtained in the present study corresponds to capillary sorption in microvoids of a radius equal to $1 \mu\text{m}$, i.e., the very high end of the range of microvoid radii as defined in Table 1. The results therefore can be interpreted as though capillary condensed water in microvoids plays at most a modest role with regard to EMC reached through desorption.

Theoretical calculation of capillary condensation in microvoids

In an attempt to better understand the sorption isotherm for untreated wood presented in Figure 1a, a theoretical calculation of the contribution from capillary condensation in the 99.0–99.9% RH range was undertaken based on the Kelvin equation and idealized microstructural geometries. These derivations and calculations are shown *in extenso* in Part 2 of this article. The result of the theoretical exercise was that the effect of capillary sorption in microvoids is expected to be insignificant with regard to the overall MC of wood even

at very high RH, below 0.35% moisture at 99.9% RH. This result supports the validity of the isotherm for untreated wood recorded and shown in Figure 1.

Modified wood

Figure 1a also illustrates that, as expected, the EMCs of the acetylated samples are systematically lower than those of the untreated samples. But more interestingly, the moisture ratio $MR_A = EMC_A/EMC_U$ between the EMCs of the acetylated and the untreated samples is more or less independent of RH. As can be seen in Figure 2a, MR_A is approximately 0.48 throughout the entire range of RH from 92% to approximately 99.6%. This result is in the same range as results for similar WPG by Papadopoulos and Hill (2003) shown in Figure 2b. Based on the hypothesis on MR_A presented in the introduction, MR_A should increase significantly with increasing RH if capillary condensation took place in both sample types. The inference of the constant moisture ratio MR_A , as seen in Figure 2a, is therefore that for desorption isotherms for untreated wood as well as for acetylated wood, capillary condensed water does not contribute to sorption below 99.9% RH.

The moisture ratios ($MR_F = EMC_F/EMC_U$) for the furfurylated samples are presented in Figure 3. For RH below 96%, the moisture ratio is of the order $MR_F = 0.8$, indicating that the furfurylated samples at equilibrium contain 80% of the water present in untreated samples at the same RH levels, i.e., in spite of a much higher WPG, furfurylation was not as effective as acetylation. Above 96% RH the MR_F gradually increases. For $RH > 99\%$, $MR_F > 1$ indicating that at such high RH, furfurylated wood could hold significantly more water than untreated wood. At $RH = 99.9\%$ untreated wood holds approximately 40% moisture, whereas furfurylated wood holds 50–60% moisture. The results of the present study confirm the findings of Venås (2008) who established adsorption isotherms for furfurylated Scots pine

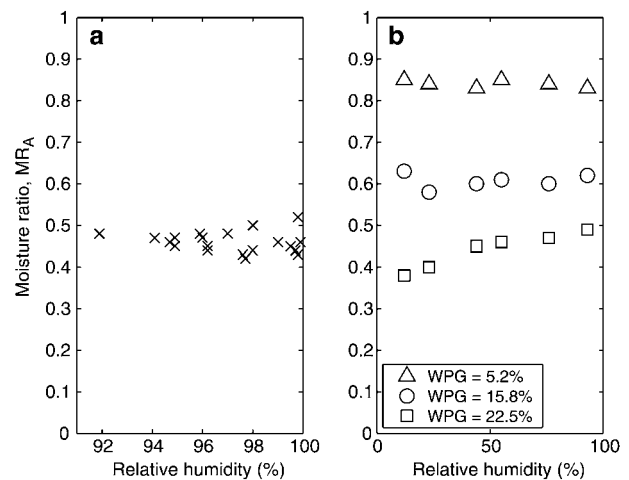


Figure 2 Moisture ratios (MR_A) for acetylated samples. (a) Results from the present study. (b) Samples acetylated to obtain a WPG of 5.4% (triangles), 15.8% (circles), and 22.5% (squares) (Panel b is based on data from Papadopoulos and Hill 2003).

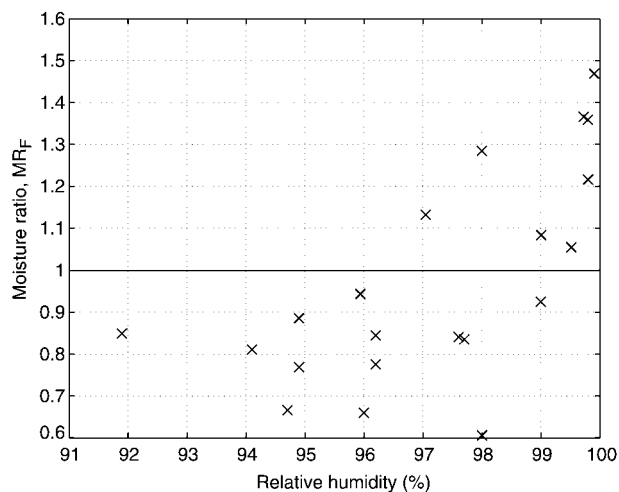


Figure 3 Moisture ratios (MR_F) as a function of relative humidity (RH) for furfurylated samples.

samples with a WPG of approximately 28%. Below $RH=85\%$ the MR_F stayed at an almost constant value of approximately 0.56. However, somewhere in the interval $85\% < RH < 100\%$ the moisture ratio started to increase to eventually reach a value of approximately $MR_F=1.0$ at a RH value characterized as 'close to 100%'. At the very high WPG levels in the present study, it is probable that the cell walls were bulked to such an extent that they were damaged and/or that the cell lumina of some cells were (partially) filled. The cause of the change in sorption behavior of furfurylated wood compared with untreated wood can thus be related to (1) sorption of the FAP itself, (2) an increase in accessibility of the sorption sites caused by less effective blocking by the FAP, or (3) capillary condensation in cracks created by the bulking of the cell wall.

Venås (2008) exposed ground FAP, i.e., the glassy, hydrophobic polymer formed by *in vitro* homopolymerization of furfuryl alcohol to saturated water vapor. The EMC was 2.6%. For the furfurylated samples in the present study with a WPG of 63%, this amount of water corresponds approximately to 1.6% moisture bound in the FAP phase. Firstly, this is a very modest contribution, and secondly there is nothing to indicate that this polymer differs from most polymers with regard to showing smooth running isotherms with no particular increase of water uptake at very high RH. The results presented in Thygesen et al. (2009) indicate that the same homopolymer is formed inside the wood. Thus, water uptake in the FAP itself does not offer a likely explanation.

Increasing the MC causes the molecular mobility of the hemicelluloses to increase (Salmén 1982; Olsson and Salmén 1997). It might therefore be hypothesized that such softening makes access to blocked sorption sites easier. However, such a mechanism would be expected to show over a considerable range of RH and not to be confined to a narrow range of the very highest RH values. In addition, such a mechanism would be incapable of explaining moisture uptake in excess of that of untreated wood. Consequently, softening can at best offer part of the explanation.

Capillary condensation can offer a better explanation. In fact, a crossing at high RH of sorption isotherms, as seen for untreated wood and furfurylated wood, is also known from other types of wood modification. Heat treatment reduces the number of available sorption sites particularly by decomposing hemicelluloses. This results in a reduced moisture sorption at intermediate levels of RH. However, the decomposition of hemicelluloses also creates voids, which result in increased moisture uptake as a result of capillary condensation at high levels of RH (Hoffmeyer et al. 2003). A related mechanism is suggested for furfurylated wood with high WPG. Water sorption is reduced by furfurylation blocking the access to sorption sites at normal levels of RH. At high levels of RH, capillary sorption in microvoids becomes active. We suggest that the microvoids are generated by the pressure impregnation with furfuryl alcohol. They might show as microcracks emerging from the bulking of the cell wall or as microvoids between cell wall matter and bulk FAP deposited, e.g., in cell lumens. The RH range from $RH=99.0\%$, where $MR \approx 1$ up to $RH=99.9\%$, which is the highest RH value of the study, corresponds to capillary radii in the range $0.1\text{--}1.0\ \mu\text{m}$. An exploratory attempt to identify such microvoids by environmental scanning electron microscopy (ESEM) was unsuccessful, perhaps because the microvoids are shut at the insufficient moisture conditions available in the ESEM (results not shown). The ESEM did, however, reveal that the lumina of ray cells were filled to some extent by the FAP.

If the marked increase of the sorption isotherm of furfurylated wood at high RH is related to capillary sorption, it would be expected that such behavior is reflected by the swelling of the wood. Either the wood will exhibit a slightly negative swelling as a result of capillary forces or a low or zero swelling caused by the filling of existing voids in the structure. Thus, the ratio of swelling over MC would decrease in the region where the sorption isotherm changes. It remains unresolved whether this is the case.

Freezing and non-freezing water as detected using LF TD NMR

The LF TD NMR method is an alternative to swelling experiments for the study of the state(s) of water in wood, i.e., for answering the question to what extent the water is 'bound' or 'free'. The method is suited for measurements both above and below the freezing point of the 'free' water. Figure 4 shows the mean free induction decay (FID) relaxation curve for the three sample types measured at $+20^\circ\text{C}$ and at -20°C . The figure demonstrates that only the mean relaxation curve of the furfurylated wood is affected by freezing the samples. This indicates that on average only the furfurylated samples contained freezing water. To make sure that the difference seen was not simply an effect of a difference in average MC between sample types, a principal component analysis (PCA) was carried out of all FIDs recorded. The PCA included data for all three sample types (untreated, acetylated, and furfurylated) and for two measurements per sample ($+20^\circ\text{C}$ and -20°C). To avoid clutter, the scores plot for factors 1 vs. 2

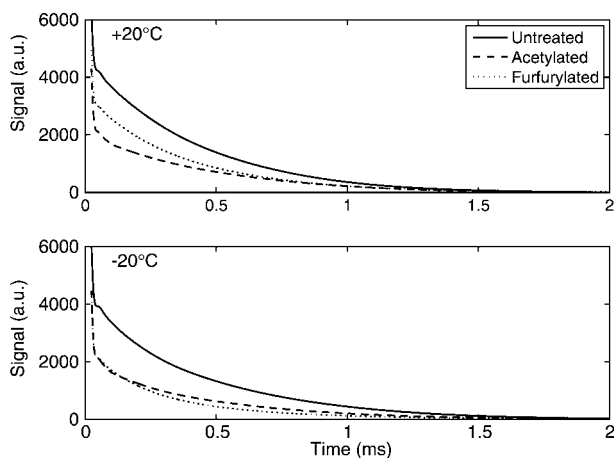


Figure 4 Mean free induction decay (FID) relaxation curves from LF TD NMR of 36 samples of each of the three sample types (untreated, acetylated, and furfurylated) at +20°C and at -20°C. Data for different moisture contents have been pooled.

for this PCA are presented as three subplots (Figure 5a,b,c), each showing data for one of the three sample types. Furthermore, the two points corresponding to the same sample are connected by a line and a circle shows which end of the line corresponds to -20°C. It is obvious that the untreated and the acetylated samples form groups that are separate from each other, regardless of the temperature. Within each of these two groups, no systematic effect of the temperature can be discerned. Contrary to this, the furfurylated samples at the -20°C group (situated within a narrow area) are well separated from the position of the samples at +20°C. At +20°C they are positioned more or less with the untreated samples, at -20°C they are positioned close to the acetylated samples.

Figure 6 shows the length of the ‘vectors’ in Figure 5 vs. the MCs of the samples. This plot demonstrates for the furfurylated samples that the higher the MC the longer the ‘vector’, i.e., the more was the FID at -20°C different from the FID at +20°C. Accordingly, the difference in signal is related to the amount of freezing water. This trend is not seen for the two other sample types indicating that they did not contain any significant amounts of freezing water. According to Petrov and Furó (2009), water in cylindrical pores with a radius down to 3 nm will freeze at -20°C. This indicates that also water in very large clusters – as those that might exist around charged groups at RH levels close to 100% – could freeze at this temperature, but so large clusters are not found around uncharged groups such as hydroxyl groups (Berthold et al. 1996). Charged (carboxylic) groups exist only in acetylated wood, not in untreated or furfurylated wood. However, no freezing occurred in the acetylated wood. Consequently, we find it probable that the water that froze in the furfurylated samples was capillary condensed water (perhaps in damaged cell walls), i.e., free water and not freezing bound water.

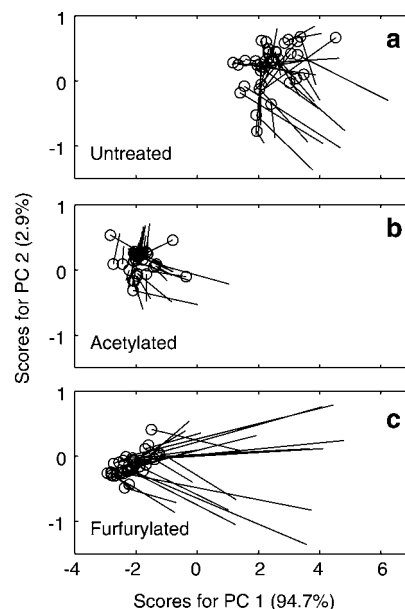


Figure 5 Principal component analysis of the 3 (sample types) × 36 (samples) × 2 (temperatures) = 216 FID relaxation curves summarized in Figure 4. Scores for factor 1 vs. scores for factor 2 are shown in three separate subplots to avoid clutter, i.e., one subplot per sample type. Within each subplot each line connects the position of a sample at +20°C with its position at -20°C (marked by a circle).

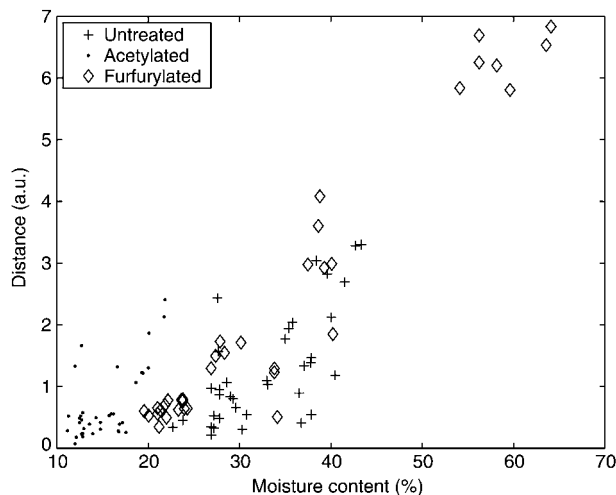


Figure 6 The distances in the PCA scores plot between the positions at +20°C and at -20°C (as seen in Figure 5) vs. the moisture content of the samples at +20°C.

Conclusions

Desorption isotherms at 20°C for untreated, acetylated, and furfurylated Norway spruce sapwood were established in the 91.9–99.9% RH range. The curve for the untreated samples did not show an upward bend, except perhaps above 99.5% RH, indicating that – contrary to what has hitherto been assumed – capillary condensation does not play a significant

role for water sorption in wood below fiber saturation. Three additional results from the present study point in the same direction:

- The theoretical contribution of capillary condensation to the MC in wood – based on idealized microstructural geometries – was calculated by the Kelvin and Laplace equations. Only very small contributions to the EMC were found, namely below 0.35% moisture at 99.9% RH.
- The moisture ratio between acetylated and untreated samples did not show an increasing trend for increasing RH, as would have been the case if capillary condensation had taken place in both untreated and acetylated wood.
- Low field time domain NMR results showed that only the relaxation curves from the furfurylated samples were affected systematically by freezing, indicating that neither untreated nor acetylated wood contained significant amounts of capillary condensed water.

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