<https://helda.helsinki.fi>

Changes in the hygroscopic behavior of cellulose due to variations in relative humidity

Lovikka, Ville A.

2018-01

Lovikka , V A , Rautkari , L & Maloney , T C 2018 , ' Changes in the hygroscopic behavior of cellulose due to variations in relative humidity ' , Cellulose , vol. 25 , no. 1 , pp. 87-104 . <https://doi.org/10.1007/s10570-017-1570-9>

<http://hdl.handle.net/10138/258246>

<https://doi.org/10.1007/s10570-017-1570-9>

Downloaded from Helda, University of Helsinki institutional repository.

This is an electronic reprint of the original article.

This reprint may differ from the original in pagination and typographic detail.

Please cite the original version.

1 Has been published in: Cellulose (2018) 25: 87-104
2 <https://link.springer.com/article/10.1007%2Fs10570-017-1570-9>

3 Changes in the hygroscopic behavior of cellulose 4 due to variations in relative humidity

5 *Lovikka, Ville A.;**[§] *Rautkari, Lauri;** *Maloney, Thaddeus C.**

6

7 * Aalto University, School of Chemical Technology, Department of Forest Products Technology,
8 P.O. Box 16300, FI-00076 Aalto, Finland

9 [§] Department of Chemistry, A.I. Virtasen Aukio 1, P.O. Box 55, FI-00014 University of Helsinki,
10 Finland

11

12 **Corresponding Author**

13 * ville.lovikka@helsinki.fi, +358-50-4989984; Orcid: 0000-0001-5412-9481

14

15 **KEYWORDS** cellulose, water adsorption, solvent exchange, hornification, surface restructuring,
16 critical point drying

17

18

19 Abstract

20 Details on how cellulosic surfaces change under changing moisture are incomplete and even
21 existing results are occasionally neglected. Unlike sometimes reported, water adsorption is
22 unsuitable for surface area measurements. However, water can be utilized for assessing surface
23 dynamics. Hygroscopic changes of pulp and bacterial cellulose were studied by dehydrating the
24 samples in a low polarity solvent and then introducing them into a moist atmosphere in a
25 Dynamic Vapor Sorption (DVS) apparatus at 0-93 % Relative Humidity (RH). The DVS
26 treatment caused hygroscopicity loss near applied RH maxima, however, the hygroscopicity
27 increased at RH values > 10-20 % units lower. Additionally, the hygroscopic changes were
28 partially reversible near the RH maximum. Therefore the hygroscopicity of cellulose could be
29 controlled by tailoring the exposure history of the sample. Hornification reduced these changes.
30 The observations support reported molecular simulations where cellulose was shown to
31 restructure its surface depending on the polarity of its environment.

32

33

34 Introduction

35 An understanding of the behavior of cellulose under conditions of changing humidity is
36 important for its applications as the hydration of cellulose, for example, reduces its adhesion and
37 dimensional stability in composites (Hubbe et al. 2008; Siró and Plackett 2010). Although

cellulosic composites often need to resist physical changes over repeated exposure events at high and low humidities, research on cellulose behavior under repeated cycling has focused on the effect of water at or near its saturation point. In order to understand more fully the intricacies of the biopolymer, more detailed studies that focus on its behavior at subsaturation humidities are needed. One such topic is the drying of cellulose, which is a complex process that leads to an irreversible reduction in swelling and surface availability, known as hornification (Minor 1994). This, hornification, in turn reduces the reactivity of pulp (Khanjani et al. 2017; Nelson and Oliver 1971; Grethlein 1985) especially with repeated drying cycles (Leuk et al. 2015) due to irreversible microfibril aggregation or ‘stiffening of the lignocellulose matrix’ (Hult et al. 2001; Newman 2004; Suchy et al. 2010a and 2010b).

Cellulose behavior and its surface properties are defined by the prevalence of available hydroxyl groups (Dufresne 2012). Cellulose molecules consist of glucopyranose rings that have their hydroxyl groups oriented in equatorial positions whilst nonpolar C-H bonds are aligned in axial directions (Fernandes et al. 2011; Yamane et al. 2006). Moreover, cellulose molecules are partially ordered in crystalline structures that possess both hydrophobic and hydrophilic surfaces (Dufresne 2012; Medronho et al. 2015; Sinko et al. 2015). At the sub-micron level, cellulose is further organized into fibrillar structures that have a more disordered surface (Fernandes et al. 2011; Maurer et al. 2013) which have more potential for outward-directed hydroxyl groups when compared to perfect crystals. Research performed with liquids has shown that a non-polar environment causes a reduction in the hydroxyl group accessibility via different effects, for example, the hydroxyl groups can adsorb impurities from the environment, reorient themselves away from the fibril surface or create cross-linkages and aggregations (Yamane et al. 2006;

61 Johansson et al. 2011). Correspondingly, exposure to polar liquids has been shown to increase
62 hydrophilicity (Bledzki and Gassan 1999) for the time of exposure despite the impact of
63 hornification. Nevertheless, it would be beneficial to be able to distinguish between the effects of
64 hornification and hygroscopic changes and to ascertain how permanent such changes are.
65 Furthermore, cellulosic samples behave very differently < 96 % relative humidity (RH) when
66 compared to that observed at levels above 96 %. Differences in water adsorption between
67 different samples has been shown to be very small below 96 % RH and occasionally not even
68 consistent with results at 99.98 % RH (Stone and Scallan 1967). This limits the applicability of
69 research results achieved at water saturation to very specific conditions.

70

71 Structurally, it is estimated that there is a thin layer of non-crystalline cellulose on the surfaces of
72 fibrils (Atalla et al. 2008; Fernandes et al. 2011; Leppänen et al. 2009; Salmén and Bergström
73 2009; Weatherwax 1977) that could be prone to hornification and interfibrillar hydrogen bonding
74 to either cellulose or hemicellulose (Leppänen et al. 2009; Mohan et al. 2012). Modeling studies
75 on a molecular level have also suggested that intrafibrillar restructuring can take place within the
76 first molecular layers (Heiner et al. 1998; Matthews et al. 2006; Maurer et al. 2013), however,
77 the nature and extent of such restructuring depend on the amorphous fraction and crystal
78 structure of the surface (Kulasinski et al. 2017; Liao et al. 2012; Yamane et al. 2006). Figure 1
79 shows the possible changes including surface irregularities and hydrogen bond changes (red
80 lines) from inter-chain (bulk cellulose, Fig. 1a) into inter-sheet bonds both in vacuum (Fig. 1b)
81 and water (Fig. 1c) (Maurer et al. 2013). There is more inter-sheet bonding against vacuum (b)
82 than against water (c) because water is able to attract hydrogen bonds. These type of structural
83 changes lead to changes in the available hydroxyl groups on the fibril surface and therefore alter

the overall hygroscopicity of the cellulose. Importantly, if there is any delay or hysteresis in the surface restructuring, the surface could also have different configurations depending on what kind of environment they have been exposed to before the actual experiments.

Fig. 1 Cross sections of cellulose I α (100) in different environments. Some of the intra-sheet hydrogen bonds, which are typical to a) bulk cellulose, restructure into inter-sheet hydrogen bonds at the surface when the surface is exposed to b) vacuum or c) water. There are more hydroxyl groups pointing outward in water than in vacuum because water can attract hydrogen bonds. The figure is from Maurer *et al.* (2013) with permission from Springer

Critical point drying (CPD) with CO₂ can be used as a method to prepare dry cellulose with relatively intact pore structures in order to analyze the porosity, surface area and microscopic structure (Lovikka et al. 2016). While CPD is commonly employed together with N₂ sorption techniques, use in conjunction with water sorption studies is much more limited. In this study, we want to determine how the CPD procedure affects the water sorption characteristics of pulp fibers over a wide RH range, especially as the CPD method at least partially prevents hornification upon water removal. The CO₂ treatment may also cause surface molecule reorientation (Johansson et al. 2011) due to the low-polar nature of the treatment. Additionally,

the treatment has been previously shown to cause changes in the molecular distances on the cellobiose unit level when compared to interactions with water (Bazooyar et al. 2015).

The main aim of this study is to understand how cellulose surfaces behave as relative humidity (i.e. water activity) is changed below its saturation point by using CPD in combination with Dynamic Vapor Sorption (DVS). In this paper, we show that the subsaturation RH behavior of cellulose is more complex than is sometimes assumed as cellulose surfaces can both gain and lose hydrophilicity with only small changes in humidity. This can have a profound impact on the reliability of both cellulose analysis methods and applications. Differently predried samples were studied to understand to what extent the hygroscopicity of cellulosic surfaces can be changed by surface restructuring, how stable these changes are and whether hornification can be used to prevent such changes.

Materials and methods

Samples and solvents

Various bleached pulps were used for the study as shown in Table 1. “Never dried” samples (ND) were never dried prior to the solvent exchange and Critical Point Drying (CPD) protocol. Other samples were either dried in 100 °C (“oven dried”) overnight or were acquired as regular

123 industrial pulp sheets (“machine dried”). These samples with different drying histories (“predried
 124 samples”) underwent cold redispersion to water before being subjected them to the same solvent
 125 exchange and CPD protocol. The K-100-Ref in the Table 1 is similar to sample K-100 except
 126 that it was not redispersed or CPD treated. Samples primarily comprised of fully bleached birch
 127 (*Betula spp.*) pulp with the addition of a sample of bacterial cellulose (from *Gluconacetobacter*
 128 *medellensis*). The bacterial cellulose (BC) preparation method has been described elsewhere
 129 (Castro et al. 2012). Acetone (VWR International) was at least of 99.5 % purity, CO₂ (Oy Aga
 130 AB) was of at least 99.8 % pure and deionized water was used throughout the experiments.

131

132 **Table 1.** The samples used in this study. All the pulp samples were bleached. N.B. the table is
 133 partially taken from Lovikka *et al.* (2016) with permission from Elsevier

Name	Species	Type	Drying	Hemicellulose content (%)
d-ND	birch	dissolving	ND	6.6
d-d	birch	dissolving	machine dried	6.0
d-100	birch	dissolving	oven (100 °C)	6.1
K-ND	birch	kraft	ND	26.1
K-100	birch	kraft	oven (100 °C)	26.0
K-100-Ref	birch	kraft	oven (100 °C)	26.1
BC	<i>G. medellensis</i>	bacterial	ND	0

134

135

136

137 Solvent exchange and critical point drying

138 Pulp samples (with 10 % solid content) were placed into 50 kDa molecular weight cut-off
139 (MWCO) regenerated cellulose membrane tubings and the pulp was solvent exchanged by
140 dialysis with acetone for over 45 hours in the presence of a magnetic stirring. The acetone was
141 subsequently exchanged with liquid CO₂ in a critical point drier (Leica EM CPD300) over 25
142 CO₂ partial exchange cycles which lasted 1 hour in total. Next the CO₂ was heated to 35°C under
143 ~75 bar pressure in order to bring it into the supercritical state and this fluid was slowly vented
144 out until only carbon dioxide gas at atmospheric pressure remained for the fluid phase. After
145 CPD was complete, the samples were immediately transferred either to DVS or the N₂ sorption
146 apparatus following the method described previously (Lovikka et al. 2016).

147

148 Dynamic Vapor Sorption (DVS)

149 H₂O sorption was measured with a Dynamic Vapor Sorption equipment (DVS Advantage ET,
150 Surface Measurement Systems). The weight of the sample was monitored with a microbalance
151 whilst a constant flow of nitrogen of predetermined water content was used to control the RH
152 within the sample chamber. The sorption-desorption isotherm cycles were collected sequentially
153 for the same sample and the sample Equilibrium Moisture Content (EMC) was recorded after the
154 mass change rate stayed below 0.002 %/min continuously over a 10-minute period. The device
155 was equipped with a calibrated RH sensor (Rotronic HC2-IC, Switzerland) that allowed the true
156 RH in the chamber at each step to be recorded. These results showed that the measured value
157 was 1-2 % units lower than the set value. The measured RH values are used in the later sections.
158 The temperature within the sample chamber was kept constant at 24 °C (±0.05 °C) and the setup
159 was additionally enclosed by an insulating box.

160

161 The measurement protocols comprised of either a 2-cycle or multicycle step process. For the 2-
 162 cycle measurements, the target humidity was increased both times in 5 % increments from zero
 163 to 95 % RH with two additional steps during the adsorption phase at 2.5 % and 7.5 % (see for an
 164 example isotherm Fig. 2a). The multicycle runs (d-ND-g and K-ND-g) were performed using a
 165 more complex program. Dissolving pulp (d-ND-g) was measured using a first cycle with a
 166 maximum at 20 % RH. Each subsequent cycle carried out was 10 % RH higher than the previous
 167 maximum until a cycle at RH 90 % was completed. After that the sample was exposed and dried
 168 from 95 % RH without intermediate steps before one more full cycle with intermediate steps to
 169 90 % RH was completed. These cycle maximum values are presented in Table 2 in chronological
 170 order. Data was only collected at every 10 % RH increase with the exception of an additional
 171 measurement step at 5 % RH. For the kraft pulp sample (K-ND-g) cycles 60 % and 70 % RH
 172 were repeated after the first exposure to 70 % RH. The last cycle of K-ND-g was set to 95 % RH
 173 instead of 90 % used for d-ND-g.

174

175 **Table 2.** The progressively higher cycles in the DVS measurements. Cycles with * were
 176 completed without any intermediate steps (0% → 95% → 0% RH)

SAMPLE NAME	RH AT EACH CYCLE MAXIMUM (%)
d-ND-g	20, 30, 40, 50, 60, 70, 80, 90, 95*, 90
K-ND-g	20, 30, 40, 50, 60, 70, 60, 70, 80, 90, 95*, 95

177

178 The specific surface areas were determined with both N₂ and H₂O. Measurements with water
179 were analyzed with the Guggenheim-Anderson-de Boer method (GAB), which can be applied
180 over a more extended range when compared to the classical BET equation (Brunauer et al. 1938;
181 Timmermann 2003). GAB was chosen, since water sorption on cellulose is specific at low RH
182 and there is no well-defined cellulose surface when water is used as the probe molecule, which
183 means that the BET method is ineffective for such H₂O sorption studies (Greyson and Levi
184 1963). Nevertheless, both methods are still being used and therefore they need further
185 examination (Häggkvist et al. 1998; Ioelovich and Leykin 2011; Espino-Pérez et al. 2016).

186

187 Kinetic analysis of DVS

188 The kinetics of the Dynamic Vapor Sorption (DVS) was studied with one of two methods: i)
189 Parallel Exponential Kinetics (PEK) model or ii) simply comparing the lengths of each sorption
190 step. The PEK method assumes two parallel, independent first order processes and relies on the
191 following parallel exponential equation (Kohler et al. 2006):

$$192 \quad M_t = M_{inf1} (1 - e^{-t/t_1}) + M_{inf2} (1 - e^{-t/t_2}) \quad (1)$$

193 where M_t is the sample mass at a given time t , M_{inf} mass at equilibrium, t_1 and t_2 the time
194 characteristic times for the two sorption processes. The sensitivity of data fitting was studied by
195 comparing the results, when the first data points were masked either by 30 seconds or until the
196 maximum slope of the curve was reached. The kinetics were also studied by a simple plotting of
197 the running times of each measured step against the target relative humidity. Average sorption

rates for each step were calculated by dividing the total mass change by the total time spent for the step.

N₂ sorption

N₂ sorption was analyzed for samples before and after DVS to monitor porosity changes during the DVS treatment. Specific surface areas (SSA) were measured at 77 K by nitrogen sorption apparatus (Tristar II, Micromeritics) and the data was analyzed using a Tristar 3020 software (Micromeritics). Approximately 150 data points were collected between the relative pressure of 0 and 0.99 for the isotherms and the surface area was determined using the Brunauer-Emmett-Teller (BET) equation (Brunauer et al. 1938) at relative pressures between 0.05 and 0.35 where the BET fitting was observed to be good. The method and the results of N₂ sorption have been recently published in more detail (Lovikka et al. 2016).

Scanning Electron Microscopy (SEM)

Samples were prepared from fresh Critical Point Dried (CPD) samples although brief exposures to humid air were possible. Single fibers were pulled from the samples with carbon tape and care was taken to avoid any unnecessary fiber compression. Samples were then sputtered with a 3 to 9 nm layer of gold prior to imaging with the secondary electron detector of a Sigma VP (Zeiss) with an acceleration voltage of 1.2-1.5 keV.

218

219 Results

220

221 DVS isotherms

222 Water adsorption behavior of the samples changed over repeated cycles of DVS measurements.
223 The sorption cycles in two-cycle measurements were different from each other until the
224 desorption phase between 20-40 % RH where the two cycles coincided (Fig. 2a, steps 2 and 4).
225 Additionally, although the samples adsorbed less water during their second cycle at high RH as
226 expected due to hornification, the adsorption was significantly increased at low and medium RH
227 in comparison to the values from the first cycle (Fig. 2a, steps 1 and 3). To best of the authors'
228 knowledge, this increase in the hygroscopic nature of cellulose under relatively mild conditions
229 have not been reported previously. Remarkably, although the first cycle isotherms are often
230 compared in the literature, the differences between the same sample isotherms (Fig. 2a) were
231 sometimes larger than between the same cycle isotherms of different samples (Fig. 3a and 3b).

232

233 The same hygroscopic changes seen in d-ND were observed to proceed, although more
234 gradually, in the corresponding multicycle run, d-ND-g. In Fig. 2b the d-ND-g isotherms are
235 plotted against d-ND and it clearly shows how the d-ND-g curves largely follow the second
236 cycle of d-ND. The measurement points of d-ND-g with the largest deviations from d-ND are the
237 new RH highs, which are located between the first and second cycle adsorption curves of d-ND
238 at $RH > 50\%$ and slightly below them at $RH < 40\%$. When the next cycle of d-ND-g reached

239 the previous RH high, adsorption was always determined to be lower than the first time (Fig. 2c).
240 If the sample was exposed to and subsequently dried from a 10-20 % units higher RH, the
241 sorption started to increase again at that RH. At humidities < 40 % RH the highest EMC
242 (Equilibrium Moisture Content, %) was reached only after 3 or more adsorption cycles to higher
243 RH values. This was counter intuitive since cellulose is generally known lose its initially porous
244 structure (Fig. 2d) upon exposure to water and as a result the sample would have been expected
245 to adsorb the most water during the first cycle.

246

247

Fig. 2 DVS isotherms. a) Whole isotherms of d-ND and comparisons (inset) to the corresponding N₂ adsorption isotherms. The units for the x- and y-axis in the inset are % and ml/g, respectively. b) Nine adsorption branches of d-ND-g (red lines, “C1-C9”) compared to the 2 cycles of d-ND (black, “C1-C2”). c) EMC values of d-ND-g presented as columns. d) SEM image and a photograph (inset) of a d-ND sample. Scale bar is 2 μm. N₂ isotherm details in a) are reprinted with permission from Elsevier (Lovikka et al. 2016)

Reversibility of the changes during repeated cycling

256 A multicycle run, with K-ND-g, was performed in a similar fashion to that for the d-ND-g
257 sample. The main difference was that for the K-ND-g the measurement cycles to 60 % and 70 %
258 were repeated after the first adsorption cycle to 70 % RH (Fig. 3c). During this repetition, the
259 adsorption of K-ND-g showed increasingly complex hygroscopic changes as the measurement
260 approached the exposure maximum. At 18 % RH, the repeated cycles did not result in any
261 notable change. At 28 and 38 % RH, the adsorption was increased after the first exposure cycle
262 to 59 and 69 % RH, however, the second exposure to 59 % resulted in a slight reduction in
263 adsorption whereas the second exposure to 69 % RH returned it to the level observed prior to the
264 repetition cycles. In other words, the exposure to 59 % RH seemed to cause the adsorption to
265 converge towards some value whereas 69 % RH only leads to increased adsorption. At 48 % RH,
266 the sorption was lowered by both cycles to 59 % RH but increased with the cycles to 69 % RH.
267 In contrast, at 59 % RH the sorption was smaller after both cycles to 59 % RH and the first to 69
268 % RH but was larger after the second exposure to 69 % RH, whereas the adsorption at 69 % RH
269 was reduced even after the second cycle to 69 % RH. After the repetition cycles, an exposure to
270 79 % RH was needed to reach new EMC maxima below 69 % RH.

271

Fig. 3 DVS isotherms. a) First cycles of the ND samples, SEM image of BC as an inset; b) second cycles of the ND samples, SEM image of K-ND as an inset; c) K-ND-g isotherm data presented as columns. Both scale bars represent 1 μm

Other cellulose sources: BC and kraft

In general, K-ND behaved much like dissolving pulp except that the changes to the hygroscopic nature of K-ND were smaller. Both samples adsorbed similar amounts of water even though

280 dissolving pulp possesses less hemicellulose than kraft pulp (Fig. 3). During the first cycle, d-ND
281 sorbed marginally less water than the K-ND between RH 28-79 % but had a slightly higher EMC
282 after exposure to 79 % RH, during the second cycle, d-ND sorbed less than K-ND also at high
283 RH.

284

285 Bacterial cellulose, which consists of cellulose only, showed two large differences in comparison
286 to the pulp samples (Fig. 3). During the first cycle, BC behaved in a similar manner to pulp at
287 RH 0-13 % but adsorbed water much less than pulp at 13-79 % and much more at 79-93 %.
288 During the second cycle the differences between pulp and BC below 69 % RH were significantly
289 smaller. Another BC sample was compressed into a film during the drying procedure, making the
290 interfibrillar distances smaller than in the non-compressed BC sample. The compressed sample
291 sorbed up to 12 % more water than the BC aerogel after 33 % RH but otherwise the isotherm
292 looked very similar to that of the uncompressed sample isotherm (results omitted for clarity).

293

294 The effect of predrying on the hygroscopic changes

295 The 2-cycle protocol was applied to the dissolving and kraft pulp samples with different drying
296 histories. The measured maximum sorption of the ND samples was found to be higher than those
297 of the predried samples as expected. The ND samples also showed the largest deviation between
298 the two cycles. The predried samples had first cycle adsorption curves that were intermediate
299 versions of the first and second cycles of the ND samples (Fig. 4). During the first desorption,
300 the K-100 sample approached K-ND isotherm until they intersected at 18-38 % RH, whilst the

second cycles of K-100 and K-ND were comparative. The same behavior was also observed for dissolving pulp once the sample weight loss during the first desorption cycle of d-100, possibly due to trapped solvent, was taken into account.

Predrying had a surprising effect at low RH values as samples d-100 and K-100 sorbed more water than their ND counterparts during the first adsorption phase. K-100 adsorbed 11 % more water than K-ND and d-100 adsorbed 7 % more than d-ND during the first cycle at 18 % RH. D-ND and K-ND started adsorbing more than the oven-dried samples only after RH 43 % and 59 % RH, respectively. Nevertheless, the differences with dissolving pulp may be underestimated because trapped solvent caused both d-d and d-100 to lose 0.27 % and 0.20 % of their weight during the first cycle, respectively. This difference was almost as large as the difference between d-ND and predried dissolving pulp samples during the first cycle desorption below 50 % RH. The d-100 sample behaved like d-d except that it adsorbed marginally more around 8 % RH and slightly less at > 38 % RH. Similarly, K-100 was found to adsorb more water than K-100-Ref except for the RH range between 0-18 %. During the second cycle the differences between ND samples and their oven-dried counterparts were smaller. For dissolving pulp, when the sample weight losses during the first cycle have been compensated, the difference is 2.2 and 2.3 % at 18 % RH during adsorption and desorption but increases starting from 2.6 % at 54 % RH to up to 8.9 % by 93 % RH. For kraft pulp the difference between ND and 100 was 1.1 % and 1.3 % during adsorption and desorption at RH 18 %, respectively, but the difference increased starting from 1.6 % at 69 % RH to up to 6.2 % by 93 % RH.

Fig. 4 The first cycle isotherms for the 2-cycle samples. a) Effect of predrying on dissolving pulp, detail of low RH range as inset, b) effect of predrying on kraft pulps, detail of low RH range as inset

DVS hysteresis

Hysteresis, defined here as the difference between adsorption and desorption divided by adsorption highlights the observed behavior of the different celluloses investigated at low and high RH (Fig. 5). Typical literature values for pulp hysteresis normally show upward slopes for pulp (Hill et al. 2009), natural fibers (Xie et al. 2010) and wood (Jalaludin 2011; Kymäläinen et al. 2014; Willems 2014a and 2014b) samples. The samples used in this study also had similar curve profiles in the second measurement cycle, though the first cycle hysteresis curves had a tendency to deviate from the literature curves in two ways. At low RH levels, the curves showed a secondary peak at circa 18 % RH, which is obviously due to lowered adsorption during the first DVS cycle, whereas at high RHs the samples had smaller hysteresis than the second cycle

338 curves. The hysteresis values at 18 % RH were plotted against the reported N₂ SSA values for
 339 the samples (Fig. 5b). For the pulp samples, there was an obvious correlation between the two
 340 values during the first cycle. In contrast, during the second cycle, the samples were more
 341 hornified and the hysteresis remained close to 0.79 for all the samples, indicating that more than
 342 half of the hysteresis anomaly at RH 18 % is independent of sample porosity. BC showed the
 343 largest changes in hysteresis at 38-48 % RH whereas pulp remained relatively unchanged across
 344 that range.

345

347 **Fig. 5** a) Hysteresis curves of some DVS samples. b) The hysteresis values at 18 % RH plotted
 348 against N₂ SSAs measured before the first DVS exposure. The full symbols are for the first (C1)
 349 and the empty symbols for the second DVS cycle (C2) values. The N₂ values are reprinted with
 350 permission from Elsevier (Lovikka et al. 2016)

351

Water sorption kinetics

In general, adsorption was faster than desorption (Fig. 6a) which can be seen both in the shorter step lengths and quicker sorption rates. This was especially pronounced during the first cycle at RH values $> 23\%$ where the difference between adsorption and desorption (Fig. 6a, the first inset) increased during the first cycle but subsequently reduced during the second. When adsorption and desorption rates were plotted, all the curves (except for the first sorption curve) showed a U-shaped behavior common for natural cellulosic fibers (Xie et al. 2010) (Fig. 6a, the second inset). With the exception of the first adsorption, the sorption rates decreased until 38% RH when reading the graph from the origin. The adsorption and desorption rates increased again at $> 69\%$ RH, which corresponds to EMC contents of $> 10\%$. However, it should be noted that in this work the kinetics data points $< 8\%$ RH and $> 89\%$ may not be fully comparable due to their shorter step lengths that might affect the results as previously shown for wood (Christensen 1959).

Kinetics were also analyzed using the PEK model but the method was unable to provide satisfactory results even with high R^2 values (> 0.999). If the first data points were not masked, the fitting residuals fluctuated strongly during curve fitting as observed previously by Driemeier *et al.* (2012). This fluctuation has been attributed to variations in the data, possibly because of small changes in temperature due to feedback system (Hill et al. 2012). In our measurements reservoir temperature changes were typically in the range of $\pm 0.02\text{ }^{\circ}\text{C}$ during a single exposure step. Nevertheless, the residual fluctuations were possibly magnified by the slow onset of the water adsorption as the residuals became smaller when more data points were masked before

curve fitting. Nonetheless, utilization of this method caused the coefficients t_1 and t_2 (equation 1) to increase and especially t_2 started to fluctuate across the measured RH range occasionally to an unacceptable extent. Therefore the results were considered to be too sensitive to the data pretreatment and the analysis was discontinued.

Fig. 6 Measurement running times and the rates of sorption. a) Data for d-ND. Hysteresis for both of the cycles are presented in the left side inset. The average rates of sorption are shown for each step in the right side inset. b) Data for d-ND-g

Comparison of H₂O and N₂ adsorption data

Specific surface area (SSA) determined by DVS was found to be relatively insensitive to the sample differences, meaning these measurements proved to be inconclusive with both BET and GAB methods. For example, BET and GAB analyses of DVS data gave similar SSA values

(108-149 m²/g and 135-188 m²/g, respectively) for the samples in spite of fibril aggregations, hornification and SSA differences over two orders of magnitude observed in N₂ adsorption (2nd and 4th column in Table 3).

391

Table 3. Specific surface areas by nitrogen and water adsorption. Values with * are averages from multiple measurements with standard deviation of 5-13 % ($\pm 2\sigma$) and are reprinted with permission from Elsevier (Lovikka et al. 2016)

SAMPLE NAME	N ₂ SSA (m ² /g)	H ₂ O SSA; Cycle 1 / Cycle 2 (m ² /g)	N ₂ SSA after DVS (m ² /g)
d-ND	199*	135 / 130	4.8
d-d	104*	136 / 125	4.5
d-100	85*	134 / 125	3.5
K-ND	225*	135 / ca 144	5.5
K-100	150*	149 / 136	1.7
K-100-Ref	-	122 / 137	-
BC	253	108 / 126	66.7

395

It is worth noting that in some of our samples H₂O adsorption was lower than N₂ adsorption, according both to SSA values and total volume adsorbed. For pore volume comparisons, both N₂ and H₂O isotherms were adjusted to the same units (liquid volume / sample weight) and plotted on the same graph (Fig. 2a inset). As can be seen, especially at low relative humidities, nitrogen is sorbed to a more significant degree, although this comparison is probably complicated as a result of diminishing sample volume due to the cryo conditions used during N₂ sorption. At room temperature the samples were found to be highly porous (Fig. 2d) before exposure to water (Lovikka et al. 2016).

Discussion

The hygroscopic properties of the surface were affected by water during both adsorption and desorption phases. This can be seen in the 2-cycle data where the two cycles differ from each other until they have similar desorption branches at low RH region. Similar observations have been reported for isotope labeled cellulose (Sepall and Mason 1961) and wood after thermo-modification at 220°C (Chirkova et al. 2009). With DVS the end point of changes could be located quite precisely, for example, the changes were completed for d-ND by 18 % RH during desorption of the first exposure cycle (Fig. 2a). The nature of these hygroscopic changes is later discussed more in detail based on observations on isotherm shapes, hysteresis and simple adsorption kinetics.

When samples were initially placed in the 0 % RH atmosphere, small weight losses of -3 % and -4.5 % were typically detected for pulp and BC, respectively. The presence of this additional weight could have been re-adsorbed moisture during the sample transfer. Other researchers have used more extensive protective measures (Weatherwax and Caulfield 1971) to prevent moisture re-adsorption and structural collapse. Nonetheless, the very high SSA values for kraft pulp before DVS analysis, up to 225 m²/g for birch (Lovikka et al. 2016), showed that the method used here was adequate and therefore the samples were also assumed to have preserved their surfaces in freshly dried state. Although some effect on the sample properties especially at low RH cannot be ruled out, the effect should be similar to those reported in this paper. Therefore the

effect due to the re-adsorption would be only to reduce our DVS observations in scale by pre-emptive hygroscopic changes, however, all the samples showed further changes even at the lowest measured RH's, once they were exposed to high enough RH's. In continuation to this, it is hypothesized that similar surface structure changes could continue both at low and high RH values at water activities beyond ambient room conditions, e.g. with supercritical water or water in nanoconfinement. Studying the latter could have beneficial effects on biocomposite development.

The sample equilibration times were not long enough to observe the samples in full equilibrium with vapor because cellulosic samples might not equilibrate even during 2-day long exposure steps (Glass et al. 2017). Because the full measurements would take months or years to complete, more commonly used step length protocol was applied (< 0.002 %/min over 10 min). Even the shorter steps are long enough to observe major changes in the EMC's (Glass et al. 2017; Hill et al. 2009). Additionally, because the observed differences between the samples and the cycles are large and systematic in the consistent experimental conditions, it is unlikely that the qualitative results would change even with longer step lengths. However, the reader is encouraged to keep in mind that quantitative results are dependent on the applied equilibration times.

Nature of the hygroscopic changes

The anomalously low sorption determined during the first exposure cycle may be due to surface restructuring and changes in the hydroxyl group accessibility caused by the nonpolar solvent

sample treatments (Johansson et al. 2011; Maurer et al. 2013, Yamane et al. 2006). This was possibly enhanced by the presence of supercritical carbon dioxide which is able to penetrate cellulose (Zheng et al. 1998). Importantly, the hygroscopic changes during adsorption were not limited to any specific RH range even though different phenomena dominate water adsorption at different RH's. Interestingly, the hygroscopicity could both increase and decrease even at low RH values where sorbent-sorbate interactions define the adsorption (Kulasinski et al. 2017; Sing et al. 1985), whereas hornification should only reduce the adsorption by increasing hydrophobicity through macromolecular ordering (Mohan et al. 2012) and reducing porosity (Fernandes Diniz et al. 2004). Adsorption in mesopores or swelling are unlikely as they are typical only when Equilibrium Moisture Content (EMC) is > 5 % or > 15 % RH (Grunin et al. 2015; Hill et al. 2009; Kulasinski et al. 2015, 2017; Salmén 1982). Water adsorption data remained almost unchanged even when N₂ SSA showed significant porosity loss caused by the DVS analysis, which indicates that mesoporosity changes should not affect DVS values very strongly. Although cellulose itself can exhibit strongly increasing adsorption at high humidities (Banik and Brückle, 2010; Hill et al. 2009), the upward bend at the high RH end of adsorption isotherms has previously been also attributed to the presence of hemicelluloses (Engelund et al. 2013; Köhnke and Gatenholm 2007; Oksanen et al. 1997). In the measurements outlined here, however, BC that does not contain hemicellulose nor any similar interfibrillar capillary structure due to its random fibril arrangement also showed increased amounts of water sorption at high RH. The results suggest that these changes in the samples must be at least partially independent from their capillary structures or exact chemical compositions. In comparison, the adsorption isotherm of BC changed more than that of pulp samples over repeated cycling, possibly as a result of the I α structure of BC, which is more labile than the I β cellulose in higher plants

(Dufresne 2012). Additionally, as the measurements were carried inside a closed chamber, contaminations were unlikely, therefore, the mechanism behind the hygroscopicity changes was likely due to surface restructuring in these samples.

Interestingly, the hygroscopic changes were smaller for samples with prior drying history. Since predried samples are more crosslinked and aggregated than never dried samples due to hornification, rearrangements of their surfaces into other configurations may have been restricted (Lang and Mason 1960). In other words, the hornification may have prevented surface restructuring during our low-polarity treatment and this would have helped to keep the hydrophilic moieties facing the fibril surfaces until the DVS measurements. The preventive effect against hygroscopic loss at low RH's was observed to be stronger in samples with a more severe predrying history, possibly because the hornification was less reversible in them as shown previously by Stone and Scallan (1966). Once the samples were exposed to high humidities in the DVS device, the presence of high water levels may have increased the hygroscopicity by triggering hydroxyl group reordering back towards the surface. After the first exposure cycle the never dried samples hornified as well, which can be seen in the similarities of cycle 2 isotherms between d-ND and the predried samples (Fig. 4a and its inset). Overall, a change in the hygroscopic nature and hypothesized hydroxyl group reorientations mean that the hydrogen bond pattern of cellulose would change as the samples are exposed to different humidity cycles. This might be related to the unexpectedly complex hornification and its reversibility reported recently for wood (Thybring et al. 2017). An interesting additional consequence of the hydroscopic changes of cellulose is that if hydrogen nuclei could be exchanged directly between cellulose hydroxyls without intermediate water, the change in the hydrogen bond network could create

proton transfer chains between the surface and subsurface parts of cellulose. This could be problematic for cellulose analytics, like deuterium labeling, although the authors are not aware of reported issues which could be unambiguously shown to be caused by this purely speculative phenomenon.

In general, hysteresis has been linked to various factors and therefore its interpretation is not straightforward. Hysteresis at low RH has been related to non-complete wetting at the nanoscale due to impurities (Cohan 1938), but as the sorption cycles were performed in a sealed DVS sample chamber, impurities do not explain the changes in hysteresis in different cycles. Moreover, according to Cohan, impurities should also lead to non-closed N₂ sorption curves, which was not observed previously (Lovikka et al. 2016). Also, hysteresis in the isotherms has previously been linked to the presence of hemicellulose (Engelund et al. 2013) and indeed kraft samples gave slightly more pronounced hysteresis curves than the dissolving pulps. Nevertheless, the presence of hemicellulose is unable to explain why hemicellulose-free BC gave rise to a stronger hysteresis than that observed for pulp. High sorption at low RH values has been linked to lower sample crystallinity (Mihiranyan et al. 2004) and this would suggest that the samples measured here would have lost crystallinity during the first water exposure cycle but this is contradicted by the results in the literature. The highest level of hysteresis at low RH was observed with a sample of relatively low crystallinity (Xie et al. 2011) and crystallinity has also been reported to be increased with a drying-rewetting cycle (Newman 2004), however, sample crystallinities were not analyzed as part of this study.

Additionally, hysteresis has also been linked to slow, glassy relaxation in the material (Engelund et al. 2013; Willems 2014b) as moisture induces glass transition within amorphous cellulose at room temperature when EMC > 10 % (Salmén 1982). This softening allows more sorption, which would cause an upward bend in the isotherms and the kinetic data at 70 % RH, both of which agree qualitatively with our data. This limit, at approximately 70 % RH or 10 % EMC, is also where water diffusion has been shown to increase strongly (Kulasinski et al. 2014; Topgaard and Söderman 2001; Zografi and Kontny 1986). Prior to this RH, specific sorption and water clustering around polar or charged groups (Bazooyar et al. 2015; Belbekhouche et al. 2011; Berthold et al. 1996; Cohan 1938; Kulasinski et al. 2017; Maurer et al. 2013; Newns 1973; Olsson and Salmén 2004) or a more tortuous diffusion path between the fibrils (Topgaard and Söderman, 2001) might slow down water mobility. The clustering and specific adsorption may sterically hinder water adsorption to nearby sites until there is sufficient water to create a percolating network through the sample (Kulasinski et al. 2014). Moreover, RH values above 75 % or EMCs above 9 % have been linked to void or capillary filling (Kulasinski et al. 2014; Mazeau et al. 2015). Unlike cellulose fibrils in BC, pulp fibrils are further arranged into denser cell wall structures (Fig. 2d and insets in Fig. 3) (Castro et al. 2012; Dufresne 2012; Klemm et al. 1998, 2001), which give rise to more microporosity and therefore could partially cause the larger hysteresis at RH > 74 % observed for pulp. Both constricted and non-constricted pores can cause hysteresis via various effects, including the inkbottle effect and different menisci shapes during adsorption and desorption (Cohan 1938). However, surface area (i.e. porosity) had only a limited correlation to hysteresis (Fig. 6b).

The rates of adsorption and desorption were similar for the d-ND sample except for the first adsorption cycle. This might be due to the fact that the ND samples still have numerous open pores during the adsorption phase of the first cycle (Fig. 2d, Table 3) which allows the water a rapid access inside the fiber cell walls. Interestingly, the first cycle desorption rate is already very similar to that of the second cycle although EMC was much higher during the first half of desorption in the first cycle. During the desorption the water is present on the surfaces and inside amorphous cellulose, and specifically during the first cycle desorption, as liquid in microcapillaries. Although the total volume of the water is larger during the first cycle, it is not free to move in a similar manner to the water vapor during the first adsorption but is more like liquid or surface-bound water during the second desorption, hence the desorption kinetics are more alike. When water evaporates during the first desorption, it pulls the fibrils towards each other due to capillary pressure and closes the pores as it retracts. As a result, the RH value where the EMC's of the two cycles coincide might indicate the point where this structural collapse is complete. For d-ND it was ca 23 % RH (Fig. 2a) which coincides well with the lowest RH outlined in the literature for hornification by Weise *et al.* (1996), who reported that hornification occurs at 20-75 % solids content, depending on the pulp type.

Gradual hygroscopic changes

The DVS isotherms show gradual changes in hygroscopicity as RH is changed. In the d-ND-g isotherms it can be seen that part of the hygroscopic changes related to the RH maxima already occur by the time the previous cycle to lower RH maximum was completed. For example, as the adsorption data point of d-ND-g at 79 % RH is roughly halfway between that of cycles 1 and 2

of d-ND, the previous d-ND-g cycle up to 69 % RH had resulted in approximately half of the changes, which would have been caused by one complete cycle to 93 % RH (Fig. 2b). This shows that the sample had some area that remained relatively unaffected until a sufficiently high RH was reached. Once a suitably high RH was achieved and the sample had been subsequently dried, most of the potential changes due to that particular RH for the cellulose sample were complete. Since cellulose swells and opens up as its EMC increases, the different RH values could be related to different locations in the sample. Similar conclusions on cellulose and wood (Greyson and Levi 1963; Taniguchi et al. 1978) have been reported to occur due to water returning to the same sorption sites at repeated RH levels. Taniguchi *et al.* showed that deuterium labeled hydroxyls in wood were not increased by repeating similar exposures but only after exposing the samples to increasingly high D₂O humidities. Interestingly, they observed no further changes with cycles extending above 60 % RH, which is not the case with DVS data outlined here. On the other hand, Greyson and Levi reported incremental reductions in N₂ SSA as water vapor exposure cycles were taken to incrementally higher RH's. With full DVS cycles it is possible to study factors behind these phenomena more in detail.

At least two phases could be identified in the sample responses when they were exposed to water vapor: first hydroxyl group accessibility was lowered at that RH (or "that sample location") as water penetrated and retracted from it for the first time. After the sample was exposed to 10-20 % RH units higher conditions and water penetrated deeper in the sample, the hydroxyl accessibility increased again at the earlier location (Fig. 2c). Interestingly, newly available sorption sites do not only appear near the new maximum but at all RH values > 10-20 % RH units below the new maximum. The experiment with repeated cycles at 59 and 69 % RH

supports these observations as, for example, sorption at < 40 % RH did not proceed during the repetitive cycles at 59 and 69 % RH nearly as much as when the exposure humidity was increased finally to 79 % RH. More sorption sites become accessible after a new peak RH is attained. Additionally, the results from K-ND-g suggest that hygroscopic changes are more reversible the closer the analyzed RH is to the previous RH maximum. Since the sorption stayed almost constant < 38 % RH while it was changing at 49-69 % RH during the repetitive cycles, it implies that the changes (hormification) are more irreversible in the RH values near the exposure maximum, or the corresponding sample location, after water has advanced and retracted from locations deeper within the sample.

Additionally, the kinetic data show an anomaly at 10-20 % RH units below each cycle maximum. With d-ND-g the highest RH measurement of a cycle took less time than the same RH measurement during the next one or two cycles (Fig. 6b), as if prior exposure to the exact same RH had made adsorption more difficult. This coincides well with the EMC minimum observed in the isotherms (Fig. 2c), which in combination with the longer step lengths (Fig. 6b) causes the adsorption rate to reach a local minimum at 10-20 % units below the previous RH maximum (not shown). Furthermore, also the kinetic effect was lost after the sample had been exposed to 20 % units higher RH and subsequently dried. Interestingly, the anomaly was not observed during desorption which indicates that the largest changes in water accessibility occur during adsorption.

On the SSA comparisons based on N₂ and H₂O adsorption

604 The comparison of H₂O and N₂ sorption data (Table 3) brings new arguments to the long-lasting
605 issue on whether the two methods are comparable. Firstly, strong interactions between adsorbate
606 molecules is not compatible with assumptions of monolayer coverages or BET theory (Sing
607 2014). Secondly, water has already been reported to be unsuitable for surface area
608 determinations for even rather stiff samples (Robens et al. 2004) and cellulose could be expected
609 to be worse as water can open up structures as it penetrates into soft and hygroscopic matter.
610 Such penetration creates smaller fractal like porosity or surfaces (Liao et al. 2012; Stone and
611 Scallan 1966; Strømme et al. 2003) which effectively means that there is no stable “surface” to
612 be studied due to sample dynamism as RH is being changed. This is supported by observation
613 that there were no expected changes in isotherm shape or adsorption heat at RH values where
614 water monolayer should have been completed (Greyson and Levi 1963). Nevertheless, even
615 recently researchers have been using water as a probe molecule in specific surface area analysis
616 which has shown high surface areas in comparison to typical nitrogen adsorption data (Espino-
617 Pérez et al. 2016; Häggkvist et al. 1998; Ioelovich and Leykin 2011; Klemm et al. 1998; Rowen
618 and Blaine 1947; Zografis et al. 1984). Some of the authors have even used this as a proof for
619 their conclusions on sample properties. Confusingly, there has also been attempts to correct
620 nitrogen sorption values closer to water sorption values, which may have differed even by orders
621 of magnitudes for some systems (Caurie 2012). In fact these differences might be caused by
622 different sample drying methods as N₂ adsorption is generally more sensitive to cellulose
623 aggregations than H₂O (Table 3). Especially for the most porous samples our results show
624 occasionally larger SSA values for H₂O than N₂ adsorption. This brings even more seriously into
625 question the validity of previously published arguments and conclusions on comparisons
626 between the two methods.

627

628

629 Conclusions

630 Exposing wet cellulosic samples first to low-polar liquids and then to water vapor was shown to
631 cause various hygroscopic changes. First hygroscopicity was reduced during the low-polar
632 treatment, when the initial water was removed from the samples with acetone and supercritical
633 CO₂. When the samples were subsequently exposed to water vapor, the fibrils aggregated and the
634 hygroscopicity was further reduced near the exposure maximum. Nevertheless, sample
635 hygroscopicity increased at Relative Humidity (RH) values more than 10-20 % RH units below
636 the maximum. Additionally, the increase was partially reversible in ambient conditions near the
637 exposure maximum. These changes were likely as a result of surface restructuring back to a more
638 hygroscopic form as water gradually penetrated and retracted from new locations within the
639 sample. Interestingly, hornification reduced the observed changes which suggests it can prevent
640 surface restructuring and especially prevent hygroscopic loss during the low polar treatments.
641 The procession of hygroscopic changes and hornification were observable with DVS, however,
642 water adsorption isotherms were shown to be unable to measure cellulosic surface areas,
643 therefore as a consequence the application of BET or similar methods to water isotherms is
644 strongly discouraged in cellulose studies. Additionally, the exposure histories should be reported
645 for cellulosic samples when adsorption studies are published.

646

647 ACKNOWLEDGMENTS

648 This work was a part of ACel program of the Finnish Bioeconomy Cluster FIBIC. The funding
649 of the Finnish Funding Agency for Technology and Innovation (TEKES) and the Academy of
650 Finland (POROFIBRE project) is acknowledged. Katarina Dimic-Misic is thanked for providing
651 the BC. Benjamin Wilson is thanked for proofreading. Henna Penttinen is thanked for the initial
652 literature review in her interesting undergraduate thesis on cellulose surfaces in environments
653 with different polarities. This work made use of the Aalto University Nanomicroscopy Center
654 (Aalto-NMC) premises.

655

656 Conflict of Interest

657 The authors declare that they have no conflict of interest.

658

659 REFERENCES

- 660 Atalla RH, Brady JW, Matthews JF, Ding S-Y and Himmel ME (2008) Structures of Plant Cell
661 Wall Celluloses. In: Biomass Recalcitrance. Blackwell Publishing Ltd. Doi:
662 10.1002/9781444305418.ch6
- 663 Banik G, Brückle I (2010) Principles of water absorption and desorption in cellulosic materials.
664 Restaurator 31:164–77. doi: 10.1515/rest.2010.012
- 665 Bazooyar F, Bohlén M, Bolton K (2015) Computational studies of water and carbon dioxide
666 interactions with cellobiose. J Mol Model 21:16. doi: 10.1007/s00894-014-2553-5
- 667 Belbekhouche S, Bras J, Siqueira G, Chappey C, Lebrun L, Khelifi B, Marais S, Dufresne A.
668 (2011) Water sorption behavior and gas barrier properties of cellulose whiskers and
669 microfibrils films. Carbohydr Polym 83:1740–8. doi: 10.1016/j.carbpol.2010.10.036
- 670 Berthold J, Rinaudo M, Salmén L (1996) Association of water to polar groups; estimations by an
671 adsorption model for ligno-cellulosic materials. Colloids Surfaces A 112:117–29. doi:
672 10.1016/0927-7757(95)03419-6
- 673 Bledzki AK, Gassan J (1999) Composites reinforced with cellulose based fibres. Prog Polym Sci
674 24:221–74. doi: 10.1016/S0079-6700(98)00018-5

675 Brunauer S, Emmett PH, Teller E (1938) Adsorption of gases in multimolecular layers. *J Am*
676 *Chem Soc* 60:309–19. doi: 10.1021/ja01269a023

677 Castro C, Zuluaga R, Álvarez C, Putaux JL, Caro G, Rojas OJ, Mondragon I, Gañán P (2012)
678 Bacterial cellulose produced by a new acid-resistant strain of *Gluconacetobacter* genus.
679 *Carbohydr Polym* 89:1033–7. doi: 10.1016/j.carbpol.2012.03.045

680 Caurie M (2012) A method to correct the wide discrepancy between Brunauer, Emmett and
681 Teller water and N₂ surface areas of adsorbents. *Int J Food Sci Tech* 47:2366–71. doi:
682 10.1111/j.1365-2621.2012.03111.x

683 Chirkova J, Andersons B, Andersone I (2009) Study of the structure of wood-related
684 biopolymers by sorption methods. *Bioresources* 4:1044–57.

685 Christensen GN (1959) The rate of sorption of water vapor by wood and pulp. *Appita J* 13:112–
686 23.

687 Cohan LH (1938) Sorption hysteresis and the vapor pressure of concave surfaces. *J Am Chem*
688 *Soc* 60:433–5. doi: 10.1021/ja01269a058

689 Driemeier C, Mendes FM, Oliveira MM (2012) Dynamic vapor sorption and thermoporometry to
690 probe water in celluloses. *Cellulose* 19:1051–63. doi: 10.1007/s10570-012-9727-z

691 Dufresne A (2012) Cellulose and potential reinforcement. In: *Nanocellulose - From nature to*
692 *high performance tailored materials*. Walter de Gruyter GmbH, pp 1–42

693 Englund ET, Thygesen LG, Svensson S, Hill CAS (2013) A critical discussion of the physics of
694 wood–water interactions. *Wood Sci Technol* 47:141–61. doi: 10.1007/s00226-012-0514-7

695 Espino-Pérez E, Bras J, Almeida G, Relkin P, Belgacem N, Plessis C, Domenek S (2016)
696 Cellulose nanocrystal surface functionalization for the controlled sorption of water and
697 organic vapours. *Cellulose* 23:2955–70. doi: 10.1007/s10570-016-0994-y

698 Fernandes AN, Thomas LH, Altaner CM, Callow P, Forsyth VT, Apperley DC, Kennedy CJ,
699 Jarvis MC (2011) Nanostructure of cellulose microfibrils in spruce wood. *Proc Natl Acad*
700 *Sci USA* 108:1195–203. doi: 10.1073/pnas.1108942108

701 Fernandes Diniz JMB, Gil MH, Castro JAAM (2004) Hornification — its origin and
702 interpretation in wood pulps. *Wood Sci Technol* 37:489–94. doi: 10.1007/s00226-003-
703 0216-2

704 Glass SV, Boardman CR, Zelinka SL (2017) Short hold times in dynamic vapor sorption
705 measurements mischaracterize the equilibrium moisture content of wood. *Wood Sci*
706 *Technol* 51:243–60. doi: 10.1007/s00226-016-0883-4

707 Grethlein HE (1985) The effect of pore size distribution on the rate of enzymatic hydrolysis of
 708 cellulosic substrates. *Nat Biotechnol* 3:155–60. doi: 10.1038/nbt0285-155

709 Greyson J, Levi AA (1963) Calorimetric measurements of the heat of sorption of water vapor on
 710 dry swollen cellulose. *J Polym Sci Part A* 1:3333–42. doi: 10.1002/pol.1963.100011106

711 Grunin LY, Grunin YB, Talantsev VI, Nikolskaya EA, Masas DS (2015) Features of the
 712 structural organization and sorption properties of cellulose. *Polym Sci Ser A* 57:43–51. doi:
 713 10.1134/S0965545X15010034

714 Heiner AP, Kuutti L, Teleman O (1998) Comparison of the interface between water and four
 715 surfaces of native crystalline cellulose by molecular dynamics simulations. *Carbohydr Res*
 716 306:205–20. doi: 10.1016/S0008-6215(97)10053-2

717 Hill CAS, Keating BA, Jalaludin Z, Mahrtdt E (2012) A rheological description of the water
 718 vapour sorption kinetics behaviour of wood invoking a model using a canonical assembly of
 719 Kelvin-Voigt elements and a possible link with sorption hysteresis. *Holzforschung* 66:35–
 720 47. doi: 10.1515/HF.2011.115

721 Hill CAS, Norton A, Newman G (2009) The water vapor sorption behavior of natural fibers. *J*
 722 *Appl Polym Sci* 112:1524–37. doi: 10.1002/app.29725

723 Hubbe MA, Rojas OJ, Lucia LA, Sain M (2008) Cellulosic nanocomposites: a review.
 724 *Bioresources* 3:929–80.

725 Hult E, Larsson PT, Iversen T (2001) Cellulose fibril aggregation -- an inherent property of kraft
 726 pulps. *Polymer (Guildf)* 42:3309–14. doi: 10.1016/S0032-3861(00)00774-6

727 Häggkvist M, Li T-Q, Ödberg L (1998) Effects of drying and pressing on the pore structure in
 728 the cellulose fibre wall studied by 1H and 2H NMR relaxation. *Cellulose* 5:33–49. doi:
 729 10.1023/A:1009212628778

730 Ioelovich M, Leykin A (2011) Study of sorption properties of cellulose and its derivatives.
 731 *Bioresources* 6:178–95.

732 Iwamoto S, Abe K, Yano H (2008) The effect of hemicelluloses on wood pulp nanofibrillation
 733 and nanofiber network characteristics. *Biomacromolecules* 9:1022–6. doi:
 734 10.1021/bm701157n

735 Jalaludin Z (2011) The water vapour sorption behaviour of wood, Edinburgh Napier University

736 Johansson L-S, Tammelin T, Campbell JM, Setälä H, Österberg M (2011) Experimental
 737 evidence on medium driven cellulose surface adaptation demonstrated using nanofibrillated
 738 cellulose. *Soft Matter* 7:10917. doi: 10.1039/c1sm06073b

739 Khanjani P, Väisänen S, Lovikka V, Nieminen K, Maloney T, Vuorinen T (2017) Assessing the
 740 reactivity of cellulose by oxidation with 4-acetamido-2,2,6,6-tetramethylpiperidine-1-oxo-
 741 piperidinium cation under mild conditions. *Carbohydr Polym* 176:293–8. doi:
 742 10.1016/j.carbpol.2017.08.092

743 Klemm D, Philipp B, Heinze T, Heinze U, Wagenknecht W (1998) General considerations on
 744 structure and reactivity of cellulose. In: *Comprehensive Cellulose Chemistry*. Wiley-VCH
 745 Verlag GmbH & Co. KGaA, pp 9–29

746 Klemm D, Schumann D, Udhardt U, Marsch S (2001) Bacterial synthesized cellulose - artificial
 747 blood vessels for microsurgery. *Prog Polym Sci* 26:1561–603. doi: 10.1016/S0079-
 748 6700(01)00021-1

749 Kohler R, Alex R, Brielmann R, Ausperger B (2006) A New Kinetic Model for Water Sorption
 750 Isotherms of Cellulosic Materials. *Macromol Symp* 244:89–96. doi:
 751 10.1002/masy.200651208

752 Kulasinski K, Derome D, Carmeliet J (2017) Impact of hydration on the micromechanical
 753 properties of the polymer composite structure of wood investigated with atomistic
 754 simulations. *J Mech Phys Solids* 103:221–35. doi: 10.1016/j.jmps.2017.03.016

755 Kulasinski K, Guyer R, Keten S, Derome D, Carmeliet J (2015) Impact of moisture adsorption
 756 on structure and physical properties of amorphous biopolymers. *Macromolecules* 48:2793–
 757 800. doi: 10.1021/acs.macromol.5b00248

758 Kulasinski K, Keten S, Churakov SV, Guyer R, Carmeliet J, Derome D (2014) Molecular
 759 mechanism of moisture-induced transition in amorphous cellulose. *ACS Macro Lett*
 760 3:1037–40. doi: 10.1021/mz500528m

761 Kymäläinen M, Havimo M, Louhelainen J (2014) Sorption properties of torrefied wood and
 762 charcoal. *Wood Mater Sci Eng* 9:170–8. doi: 10.1080/17480272.2014.916348

763 Köhnke T, Gatenholm P (2007) The effect of controlled glucuronoxylan adsorption on drying-
 764 induced strength loss of bleached softwood pulp. *Nord Pulp Pap Res J* 22:508–15. doi:
 765 10.3183/NPPRJ-2007-22-04-p508-515

766 Lang ARG, Mason SG (1960) Tritium exchange between cellulose and water: accessibility
 767 measurements and effects of cyclic drying. *Can J Chem* 38:373–87. doi: 10.1139/v60-053

768 Leppänen K, Andersson S, Torkkeli M, Knaapila M, Kotelnikova N, Serimaa R (2009) Structure
 769 of cellulose and microcrystalline cellulose from various wood species, cotton and flax
 770 studied by X-ray scattering. *Cellulose* 16:999–1015. doi: 10.1007/s10570-009-9298-9

771 Leuk P, Schneeberger M, Hirn U, Bauer W (2015) Heat of Sorption: A Comparison Between
 772 Isotherm Models and Calorimeter Measurements of Wood Pulp. *Dry Technol* 34:563–73.
 773 doi: 10.1080/07373937.2015.1062391

774 Liao R, Zhu M, Zhou Xin, Zhang F, Yan J, Zhu W, Gu C (2012) Molecular dynamics study of
 775 the disruption of H-bonds by water molecules and its diffusion behavior in amorphous
 776 cellulose. *Mod Phys Lett B* 26:1250088. doi: 10.1142/S0217984912500881

777 Lovikka VA, Khanjani P, Väisänen S, Vuorinen T, Maloney TC (2016) Porosity of wood pulp
 778 fibers in the wet and highly open dry state. *Microporous Mesoporous Mater* 234:326–35.
 779 doi: 10.1016/j.micromeso.2016.07.032

780 Matthews JF, Skopec CE, Mason PE, Zuccato P, Torget RW, Sugiyama J, Himmel ME, Brady
 781 JW (2006) Computer simulation studies of microcrystalline cellulose Iβ. *Carbohydr Res*
 782 341:138–52. doi: 10.1016/j.carres.2005.09.028

783 Maurer RJ, Sax AF, Ribitsch V (2013) Molecular simulation of surface reorganization and
 784 wetting in crystalline cellulose I and II. *Cellulose* 20:25–42. doi: 10.1007/s10570-012-9835-
 785 9

786 Mazeau K (2015) The hygroscopic power of amorphous cellulose: A modeling study. *Carbohydr*
 787 *Polym* 117:585–91. doi: 10.1016/j.carbpol.2014.09.095

788 Medronho B, Duarte H, Alves L, Antunes F, Romano A, Lindman B (2015) Probing cellulose
 789 amphiphilicity. *Nord Pulp Pap Res J* 30:58–66. doi: 10.3183/NPPRJ-2015-30-01-p058-066

790 Mhranyan A, Llagostera AP, Karmhag R, Strømme M, Ek R (2004) Moisture sorption by
 791 cellulose powders of varying crystallinity. *Int J Pharm* 269:433–42. doi:
 792 10.1016/j.ijpharm.2003.09.030

793 Mohan T, Spirk S, Kargl R, Doliška A, Vesel A, Salzmann I, Resel R, Ribitsch V, Stana-
 794 Kleinschek K (2012) Exploring the rearrangement of amorphous cellulose model thin films
 795 upon heat treatment. *Soft Matter* 8:9807–15. doi: 10.1039/c2sm25911g

796 Minor JL (1994) Hornification — its origin and meaning. *Prog Pap Recycl* 3:93–5.

797 Nelson R, Oliver DW (1971) Study of cellulose structure and its relation to reactivity. *J Polym*
 798 *Sci Pol Sym* 36:305–20. doi: 10.1002/polc.5070360122

799 Newman RH (2004) Carbon-13 NMR evidence for cocrystallization of cellulose as a mechanism
 800 for hornification of bleached kraft pulp. *Cellulose* 11:45–52. doi:
 801 10.1023/B:CELL.0000014768.28924.0c

802 Newns AC (1973) Sorption and Desorption Kinetics of the Cellulose and Water System - Part 2.
 803 *J Chem Soc Faraday Trans 1* 69:444–8. doi: 10.1039/F19736900444

804 Oksanen T, Buchert J, Viikari L (1997) The role of hemicelluloses in the hornification of
805 bleached kraft pulps. *Holzforschung* 51:355–60. doi: 10.1515/hfsg.1997.51.4.355

806 Olsson A-M, Salmén L (2004) The association of water to cellulose and hemicellulose in paper
807 examined by FTIR spectroscopy. *Carbohydr Res* 339:813–8. doi:
808 10.1016/j.carres.2004.01.005

809 Pierce C, Wiley JW, Smith RN (1949) Capillarity and surface area of charcoal. *J Phys Chem*
810 53:669–83. doi: 10.1021/j150470a007

811 Robens E, Dąbrowski A, Kutarov VV (2004) Comments on surface structure analysis by water
812 and nitrogen adsorption. *J Therm Anal Calorim* 76:647–57. doi:
813 10.1023/B:JTAN.0000028044.44316.ce

814 Rowen JW, Blaine RL (1947) Sorption of nitrogen and water vapor on textile fibers. *Ind Eng*
815 *Chem* 39:1659–63. doi: 10.1021/ie50456a029

816 Salmén L (1982) Temperature and water induced softening behaviour of wood fiber based
817 materials, The Royal Institute of Technology, Stockholm

818 Sepall O, Mason SG (1961) Hydrogen exchange between cellulose and water: II. Interconversion
819 of accessible and inaccessible regions. *Can J Chem* 39:1944–55. doi: 10.1139/v61-261

820 Sing KSW (2014) Assessment of Surface Area by Gas Adsorption. In: *Adsorption by Powders*
821 *and Porous Solids*, 2nd edn. Elsevier Ltd., pp 237–68

822 Sing KSW, Everett DH, Haul RAW, Moscou L, Pierotti RA, Rouquérol J, Siemieniowska T
823 (1985) Reporting physisorption data for gas/solid systems with special reference to the
824 determination of surface area and porosity. *Pure Appl Chem* 57:603–19. doi:
825 10.1351/pac198557040603

826 Sinko R, Qin X, Keten S (2015) Interfacial mechanics of cellulose nanocrystals. *MRS Bull*
827 40:340–8. doi: 10.1557/mrs.2015.67

828 Siró I, Plackett D (2010) Microfibrillated cellulose and new nanocomposite materials: A review.
829 *Cellulose* 17:459–94. doi: 10.1007/s10570-010-9405-y

830 Stone JE, Scallan AM (1967) The effect of component removal upon the porous structure of the
831 cell wall of wood. II. Swelling in water and the fiber saturation point. *Tappi J* 50:496–501.

832 Stone JE, Scallan AM (1966) Influence of drying on the pore structures of the cell wall. In:
833 *Consolidation of the paper web: Transactions of the symposium held at Cambridge*. pp 145–
834 74

835 Strømme M, Mihranyan A, Ek R, Niklasson GA (2003) Fractal dimension of cellulose powders
836 analyzed by multilayer BET adsorption of water and nitrogen. *J Phys Chem B* 107:14378–
837 82. doi: 10.1021/jp034117w

838 Suchy M, Kontturi E, Vuorinen T (2010a) Impact of drying on wood ultrastructure: Similarities
839 in cell wall alteration between native wood and isolated wood-based fibers.
840 *Biomacromolecules* 11:2161–8. doi: 10.1021/bm100547n

841 Suchy M, Virtanen J, Kontturi E, Vuorinen T (2010b) Impact of drying on wood ultrastructure
842 observed by deuterium exchange and photoacoustic FT-IR spectroscopy.
843 *Biomacromolecules* 11:515–20. doi: 10.1021/bm901268j

844 Taniguchi T, Harada H, Nakato K (1978) Determination of water adsorption sites in wood by a
845 hydrogen–deuterium exchange. *Nature* 272:230–1. doi: 10.1038/272230a0

846 Thybring EE, Thygesen LG, Burgert I (2017) Hydroxyl accessibility in wood cell walls as
847 affected by drying and re-wetting procedures. *Cellulose* 24:2375–84. doi: 10.1007/s10570-
848 017-1278-x

849 Timmermann EO (2003) Multilayer sorption parameters: BET or GAB values? *Colloids*
850 *Surfaces A* 220:235–60. doi: 10.1016/S0927-7757(03)00059-1

851 Topgaard D, Söderman O (2001) Diffusion of Water Absorbed in Cellulose Fibers Studied with
852 ¹H-NMR. *Langmuir* 17:2694–702. doi: 10.1021/la000982l

853 Weatherwax RC (1977) Collapse of cell-wall pores during drying of cellulose. *J Colloid Interf*
854 *Sci* 62:432–46. doi: 10.1016/0021-9797(77)90094-7

855 Weatherwax RC, Caulfield DF (1971) Cellulose aerogels: an improved method for preparing a
856 highly expanded form of dry cellulose. *Tappi J* 54:985–6.

857 Weise U, Maloney T, Paulapuro H (1996) Quantification of water in different states of
858 interaction with wood pulp fibres. *Cellulose* 3:189–202. doi: 10.1007/BF02228801

859 Willems W (2014a) The water vapor sorption mechanism and its hysteresis in wood: the
860 water/void mixture postulate. *Wood Sci Technol* 48:499–18. doi: 10.1007/s00226-014-
861 0617-4

862 Willems W (2014b) Hydrostatic pressure and temperature dependence of wood moisture
863 sorption isotherms. *Wood Sci Technol* 48:483–98. doi: 10.1007/s00226-014-0616-5

864 Xie Y, Hill CAS, Jalaludin Z, Curling SF, Anandjiwala RD, Norton AJ, Newman G (2010) The
865 dynamic water vapour sorption behaviour of natural fibres and kinetic analysis using the
866 parallel exponential kinetics model. *J Mater Sci* 46:479–89. doi: 10.1007/s10853-010-4935-
867 0

868 Xie Y, Hill CAS, Jalaludin Z, Sun D (2011) The water vapour sorption behaviour of three
869 celluloses: analysis using parallel exponential kinetics and interpretation using the Kelvin-
870 Voigt viscoelastic model. *Cellulose* 18:517–30. doi: 10.1007/s10570-011-9512-4

871 Yamane C, Aoyagi T, Ago M, Sato K, Okajima K, Takahashi T (2006) Two different surface
872 properties of regenerated cellulose due to structural anisotropy. *Polym J* 38:819–26. doi:
873 10.1295/polymj.PJ2005187

874 Zheng Y, Lin H, Tsao GT (1998) Pretreatment for cellulose hydrolysis by carbon dioxide
875 explosion. *Biotechnol Prog* 14:890–6. doi: 10.1021/bp980087g

876 Zografi G, Kontny MJ, Yang AYS, Brenner GS (1984) Surface area and water vapor sorption of
877 microcrystalline cellulose. *Int J Pharm* 18:99–116. doi: 10.1016/0378-5173(84)90111-X

878 Zografi G, Kontny MJ (1986) The interactions of water with cellulose- and starch-derived
879 pharmaceutical excipients. *Pharm Res* 3:187–94. doi: 10.1023/A:1016330528260

880