

# THE SWELLING AND PORE STRUCTURE OF MICROFIBRILLATED CELLULOSE

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## ABSTRACT

The aim of this work was to understand the particle level swelling and pore structure of microfibrillated cellulose (MFC). For this purpose, a new variant of the solute exclusion test was constructed which takes into account the adsorption of dextran onto the cellulosic material and the elastic response of the fiber material to external osmotic pressure. With the new method, two important properties, fiber saturation point at zero external osmotic pressure (FSP<sub>0</sub>) and isotropic elastic modulus could be obtained. The particle level swelling for MFC was found to be 1.6 ml/g which is about the same as the swelling of the parent pulp fibers. The MFC swelling was confirmed with thermoporosimetry which yielded further insights into the development of pore structure and surface area when the fiber cell wall is defibrillated.

**Keywords:** Microfibrillated cellulose, swelling, solute exclusion, fiber saturation point, isotropic elastic modulus, thermoporosimetry, hydrated surface area, pore water.

## INTRODUCTION

For water-saturated microgel systems, the water held within an individual particle is a measure of the particle level swelling. Swelling is relevant to many aspects of a material's behavior. For pulp fibers, the degree of swelling is linked to dewatering [1], recyclability [2], strength development [3] and fiber flexibility [4].

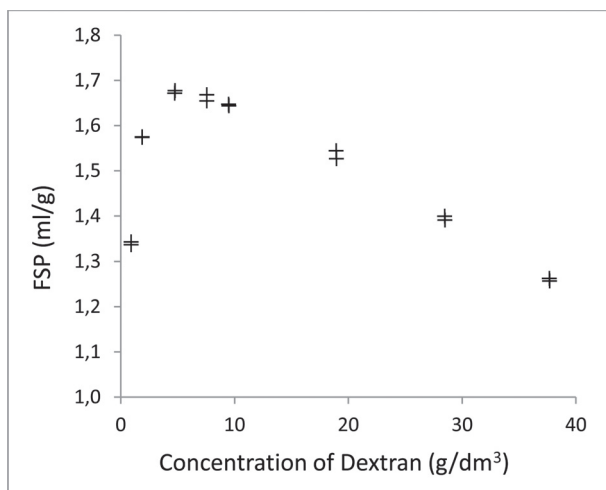
Microfibrillated cellulose (MFC) is a cellulosic material consisting of microfibril aggregates which are in turn composed of elementary microfibrils about 4–5 nm in cross-section. The main source of cellulose microfibrils is the plant cell wall, but also bacterial cellulose can be used for producing nanocellulose [5]. MFC can be produced by disintegrating low-yield pulp fibers either with purely mechanical action or with additional chemical treatments [6–11]. The diameter of individual MFC strands is usually in the size range 10–30 nm and is dependent on the raw material and processing conditions [8]. MFC has a highly truncated, entangled structure. MFC has a viscous gel-like appearance even at low solids contents and it is capable of binding a significant amount of water [6,7].

The solute exclusion technique was introduced in the 1960s [12,13]. It has been used to determine the total amount of water in the saturated cell wall of pulp fibers, defined as the fiber saturation point (FSP). In the solute exclusion test, the principle is to add a non-interacting probe molecule solution to the pulp sample and measure the dilution of the solution. If the probe molecule is so large (bigger than 30 nm for low yield pulp fibers) it cannot penetrate into the cell wall, then the inaccessible water is a measure of the total pore volume (FSP). In practice, a  $2 \times 10^6$  Dalton dextran molecule, with a spherical diameter in solution of about 54 nm, is frequently used to measure FSP. The FSP can be calculated by

$$FSP = \frac{w_{dex} + w_{water}}{w_{pulp}} - \frac{w_{dex}}{w_{pulp}} \cdot \frac{c_i}{c_f} \quad (1)$$

where  $w_{dex}$ ,  $w_{water}$  and  $w_{pulp}$  is the mass of dextran solution, water in the sample and dry pulp, respectively, and  $c_i$  and  $c_f$  are initial and final concentrations of the dextran solution. Polarimetry provides high enough accuracy to measure dextran concentration.

The solute exclusion test has been used to evaluate e.g. fiber processing [14–16] and the effect of the electrolyte environment [17] on the degree of swelling. An important assumption in the solute exclusion test is that the dextran probe does not adsorb or otherwise interact with the pulp fibers. However, Figure 1 shows that the measured FSP varies in a complex pattern as a function of dextran concentration. This indicates that dextran interacts with the cellulosic material, contrary to the test's basic assumptions. We have found that the main pattern of data in Figure 1 is similar for a range of pulp fibers and nanocelluloses.



**Figure 1.** Fiber saturation point of never-dried bleached birch Kraft pulp (Na<sup>+</sup> form) as a function of dextran concentration. Duplicate measurements at each concentration are shown.

When very low concentrations of dextran are used, the FSP will become negative. After discounting other possible explanations for this phenomenon, such as possible non-linearity in the polarimeter measurements, our conclusion is that small amounts of dextran must adsorb to the fiber surface. Although dextran is a highly soluble almost neutral polymer, and thus ordinarily it has very weak adsorption, only slight adsorption is sufficient to distort the FSP result. Other studies have found that dextran will adsorb onto other types of surfaces such as silica and steel [18,19].

Another interaction that should be accounted for in the solute exclusion test, is the osmotic pressure balance between the external dextran solution and the inside of the swollen particle. As dextran concentration is increased the increased osmotic pressure squeezes water out of the material and decreases the FSP. These two different effects, adsorption and elastic response to external osmotic pressure distort the FSP curve. This paper describes the method for correcting for these effects.

## EXPERIMENTAL SECTION

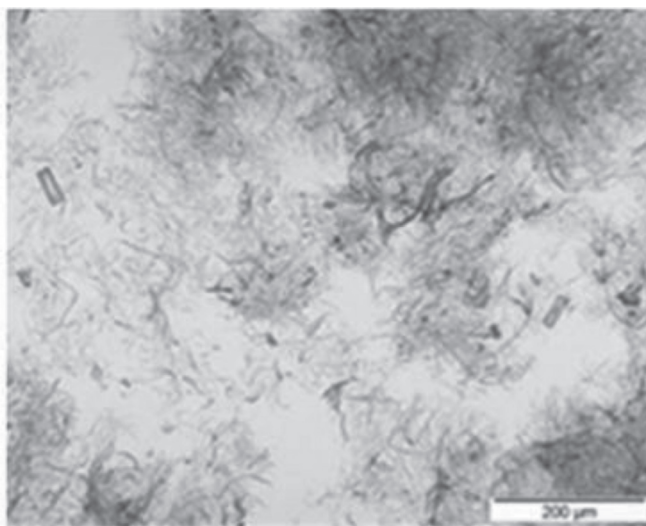
### Sample Preparation

Never-dried ECF bleached birch Kraft pulp was provided by a Finnish pulp mill. The acid groups in the pulp fibers were converted to either H<sup>+</sup>- or Na<sup>+</sup>-form.

First fibers were converted to  $H^+$ -form by adding 0.01 M hydrochloric acid (HCl) until the pH was 3.5 where it was maintained for 30 minutes. The excess acid was removed by filtration and the pulp was washed repeatedly with deionized water until the conductivity of the filtrate was less than  $5 \mu S/cm$ . A portion of the pulp was converted to the  $Na^+$ -form by soaking the  $H^+$ -form pulp in 0.01 M sodium bicarbonate ( $NaHCO_3$ ) for 10 minutes. The pH was then adjusted to 10 with sodium hydroxide (NaOH) and held constant for 30 minutes. After that, the pulp was washed repeatedly with deionized water as described above.

Some measurements (in Table 1) were done with never-dried bleached softwood Kraft pulp in no specific ionic form. In this table, the never-dried and once dried softwood pulp were also refined with Voith Sulzer refiner at 200 kWh/t. Samples referred to as either “MFC” or “parent pulp fibers” are all in the sodium form unless otherwise stated.

MFC was produced from the never-dried chemical birch pulp with a Masuko Supermasscolloider MKZA 10–15J at approximately 2% solid content. The specific energy consumption of grinding was 7.3 kWh/kg. The Brookfield viscosity of the MFC was 81 Pas measured at 1.5% solids and 10 RPM. The turbidity of the same sample was 290 NTU. An image of the MFC is shown in Figure 2.



**Figure 2.** Light microscopy images of MFC used in this study.

Before the FSP measurements, the fiber materials were thoroughly washed in order to remove optically active dissolved and colloidal substances. The optical rotation on the filtrate was measured with a polarimeter in order to ensure the washing was sufficient and the washing was continued until the optical rotation of the filtrate was 0°. The solids content of the pulp fibers was adjusted to 20% for FSP measurements, while the MFC was adjusted to 1% solids.

### **FSP Measurement**

Solute exclusion measurements were performed at varying dextran ( $2 \times 10^6$  Dalton dextran, Sigma-Aldrich) concentrations from 0.02 to 4 %. The external osmotic pressures varied over the range of 0.05–46 Pa. Each measurement was done in duplicate. 35 ml of dextran solution was added to 0.7 g (oven dried) pulp fibers and 15 ml of dextran was added to 0.3 g (od) MFC and the solutions were mixed for one hour. The solids content (mass cellulose/mass suspension) at which the test was performed was 1.8% for pulp fibers and 0.7% for MFC). The sample size had been optimized to give the highest repeatability for each type of sample, fibers or nanocellulose gel. The solution containing pulp fibers was centrifuged at 3500g and the solution containing MFC at 14000g for 10 min in order to extract the supernatant. The optical rotation of the supernatant, i.e. the final concentration of dextran after adding the cellulosic material, at a constant 20 °C was measured in a Rudolph Research Autopol IV polarimeter at 436 nm wavelength. The optical rotation of the reference dextran solution, i.e. the concentration before adding the cellulosic material, was also measured. After extracting the dextran, the fiber materials were collected and washed thoroughly, dried at 105°C and weighed in order to obtain the exact amount of dry material.

The pore size distribution from solute exclusion was done by using the above procedure, but the probe molecule was varied. Analytical grade dextran probes (Sigma-Aldrich) were used in the range from 2 M Daltons down to sucrose, covering the range from 54 to 1 nm.

### **Calculation of $FSP_0$ and isotropic elastic modulus**

When dextran is mixed with the cellulosic material, the adsorption of dextran is assumed to follow Langmuir adsorption isotherm in the form.

$$\theta = \frac{\gamma \cdot \alpha \cdot c_f}{1 + \alpha \cdot c_f} \quad (2)$$

where  $\theta$  is the fractional coverage of the surface,  $c_f$  is the final concentration of the dextran solution,  $\gamma$  is the saturation value and  $\alpha$  a parameter.

If it is assumed that the dextran does not enter the pores smaller than the hydraulic diameter of the probe molecule and that material responds elastically to the changes in external osmotic pressure, then the isotropic elastic modulus ( $E_i$ ) is described by eq. 3. Here the stress equals the osmotic pressure ( $\pi$ ), which is increased by increasing the concentration of dextran and the strain is the corresponding volumetric change.

$$E_i = \frac{\pi}{\text{Strain}} \quad (3)$$

For an ideal solution, the osmotic pressure depends on the concentration of dextran according to

$$\pi = \frac{R \cdot T}{M_n} \cdot c_f \quad (4)$$

where  $R$  is the gas constant (8.314 Nm/molK),  $T$  the temperature (293 K) and  $M_n$  the molar mass of dextran (2 000 000 g/mol).

The volumetric strain in Eq. 3 expresses the deswelling of the material, i.e. volumetric change, and it depends essentially on the osmotic pressure of the solution in which the material is immersed [20].

$$\text{Strain} = \frac{V_i - V_f}{V_i} = \frac{(V_p + V_{in_0}) - (V_p + V_{in})}{V_p + V_{in_0}} = \frac{V_{in_0} - V_{in}}{V_p + V_{in_0}} \quad (5)$$

In eq. 5,  $V_i$  is the initial specific volume of the cellulosic particle in water without dextran,  $V_f$  is the particle volume after dextran addition,  $V_p$  is the specific volume of dry pulp,  $V_{in}$  is the volume of inaccessible water and  $V_{in_0}$  is the volume of inaccessible water at 0 external osmotic pressure (= 0% dextran concentration).

Combining eqs. 2–5 yields a new swelling equation

$$c_i \cdot w_{dex} = \frac{w_p \cdot \gamma \cdot \alpha \cdot c_f}{1 + \alpha \cdot c_f} + c_f \cdot w_t + \frac{c_f^2 \cdot \frac{R \cdot T}{M_n} \cdot w_p \cdot 0.67}{E_i} + \frac{c_f^2 \cdot \frac{R \cdot T}{M_n} \cdot w_{in_0}}{E_i} - c_f \cdot w_{in_0} \quad (6)$$

where  $c_i$  is the concentration of the initial dextran solution,  $w_{dex}$ ,  $w_p$ ,  $w_t$  and  $w_{in_0}$  are the masses of dextran solution, dry fiber material, total water and inaccessible water at 0 external osmotic pressure, respectively.

Numerical solution of (6) allows one to extract two parameters of special interest; the isotropic elastic modulus,  $E_i$ , and the swelling at 0 external osmotic

pressure,  $FSP_0$  ( $FSP_0 = w_{ino}/w_p$ ). Also, an estimate of the amount of the dextran adsorbed,  $\gamma$ , can be obtained from the equation.

### **Thermoporosimetry measurements**

The thermoporosimetry measurements were done on a Mettler 821e differential scanning calorimeter (DSC). Temperature calibration was done using both mercury and twice distilled water. The temperature calibration was done using 0.02°C isothermal steps. The temperature reproducibility with this method is  $\pm 0.02^\circ\text{C}$ . The enthalpy calibration was done with a twice distilled water sample and a dynamic melting peak at 5°C/min. This gives enthalpy reproducibility better than  $\pm 1\%$ .

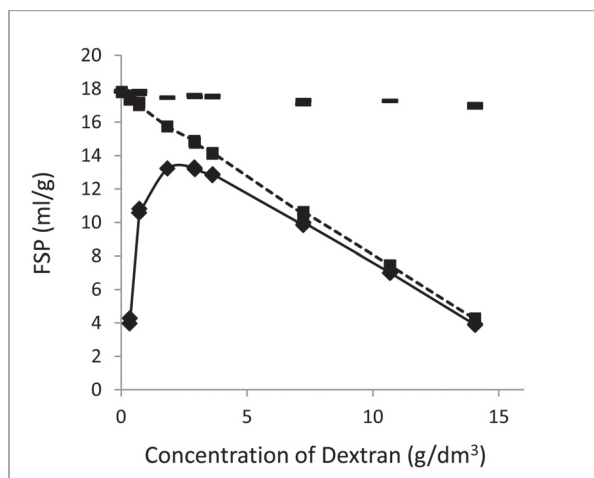
A 5–10 mg sample of pulp or MFC was sealed in an aluminum sample pan. The temperature was brought to  $-50^\circ\text{C}$  causing all the freezable water to crystallize. The temperature was then increased to  $-0.2^\circ\text{C}$  at 5°C/min and held constant until the melting transition was completed. This allows the water in small capillaries to melt, but maintains the bulk water in a frozen state, thus preventing supercooling in subsequent recrystallization.  $-0.2^\circ\text{C}$  is used as the melting temperature, since this is the highest temperature (thus largest pores) that can be obtained without interference from bulk water melting. The temperature was then decreased at 5°C/min to  $-50^\circ\text{C}$ . Integration of the resulting freezing peak allowed calculation of the freezing bound water (FBW). The temperature was then increased at 5°C/min to  $+20^\circ\text{C}$ . Integration of the resulting peak allowed determination of the total freezable water in the sample. The difference between the sample moisture content and the total amount of freezable water was used to calculate the nonfreezing water (NFW).

It is assumed that the melting enthalpy of all freezable water in the pulp or MFC samples is the same as the enthalpy of bulk water; 334 J/g. Moisture contents and pore volumes are expressed in ml/g solids, although most lab measurements are made gravimetrically. It is assumed that the density of water, including NFW, FBW and bulk water is 1 g/cm<sup>3</sup>. Any deviations from this are neglected in this study.

## **RESULTS AND DISCUSSION**

### **The $FSP_0$ and isotropic elastic modulus**

The model fit of the FSP measurements of MFC is shown in Figure 3. The figure illustrates how the model corrects for dextran sorption and osmotic pressure exerted by the dextran solution on the MFC. The  $FSP_0$  is the intercept



**Figure 3.** Model fit of FSP (2M Dalton probe) measured from MFC produced from bleached birch Kraft pulp in  $\text{Na}^+$ -form. Original FSP with fitted model (◆), data after correction for dextran sorption (■), data after correction for both adsorption and osmotic pressure (○).

of the dashed line with the y-axis. The isotropic elastic modulus ( $E_i$ ) is inversely proportional to the slope of the dashed line in the figure. The figure shows that the dextran concentration dependence is very large for a pliable swollen material such as MFC, so osmotic and adsorption effects must be accounted for.

Table 1 shows the swelling and elastic modulus data calculated for several pulp and MFC samples. The  $\text{FSP}_0$  for the pulp samples are logical and self-consistent. The  $\text{Na}^+$  form of the birch pulp has a slightly higher  $\text{FSP}_0$  than for the  $\text{H}^+$  form, hornification substantially lowers swelling and refining increases swelling. It is worth noting that the effect of the corrections discussed above to the classical FSP method is most substantial for cases where the material is highly swollen and/or fibrillated. Thus the  $\text{FSP}_0$  of refined pulps deviates somewhat from the classical FSP measurement. In this case, the  $\text{FSP}_0$  for moderately refined softwood Kraft is 2.44 g/g which compares to a FSP of 1.6 g/g for a similar pulp in an earlier study [21].

The interpretation of the  $\text{FSP}_0$  data for the MFC presents some challenges. Firstly, the Stokes diameter of the 2 Million Dalton dextran probe is about 54 nm. This is actually larger than the diameter of the MFC, which is in the range of 10–N30 nm diameter. Thus the probe molecule cannot fully access the outer surface



**Table 1.** Isotropic elastic modulus ( $E_i$ ), FSP at 0 external osmotic pressure ( $FSP_0$ ) for assorted pulp and MFC samples

<i>Sample</i>	$E_i$ (Pa)	$FSP_0$ (ml/g)
Never-dried hardwood pulp, H <sup>+</sup> -form	165	1.80
Never-dried hardwood pulp, Na <sup>+</sup> -form	208	1.83
MFC from never-dried hardwood, H <sup>+</sup> -form	25	11.6
MFC from never-dried hardwood, Na <sup>+</sup> -form	24	17.5
Never-dried softwood pulp	698	1.48
Previously dried softwood pulp	1420	1.05
Never-dried softwood pulp, refined 200 kWh/t	167	2.44
Dried softwood pulp, refined 200 kWh/t	364	1.61

area of the MFC and some interstitial water is included in the measurement (see Figure 4). This can be seen by the fact that for MFC the  $FSP_0$  is highly dependent on the solids concentration (which was kept constant at 0.7% for this study). For pulp fibers, on the other hand, the dextran probe can fully access the surface of the relatively larger diameter fibers. Thus for pulp fibers, the  $FSP_0$  is nearly independent of solids concentration.

The moduli in Table 1 seem to give an interesting measure of the pliability of the outer surface of the cell wall in the swollen state. This is important when considering bond development and consolidation issues. Drying the fiber is shown to increase the modulus, thus lowering bonding potential. Refining, has the opposite effect of decreasing the modulus allowing for greater fiber-fiber contact, surface mobility and ultimately bonding.

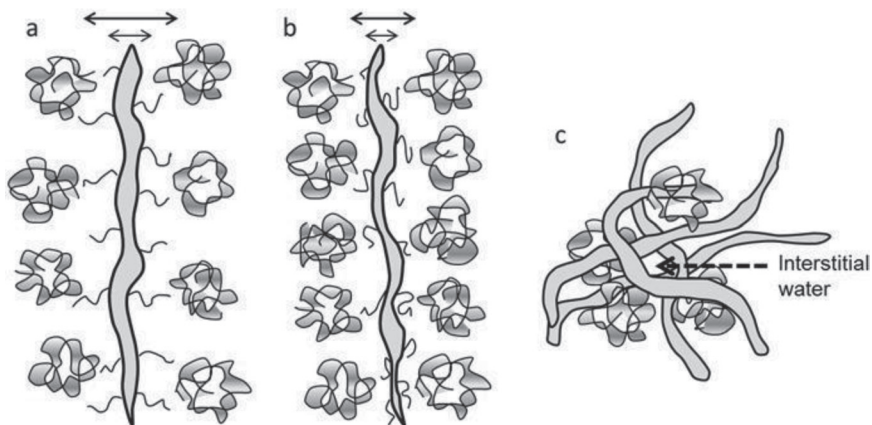
While the results in Table 1 indicate the new measurement of  $E_i$  may provide useful measure of surface modulus, one must use a degree of caution when interpreting the results. The dextran probe that is used to deform the surface is itself, soft, mobile and polydisperse. The dextran molecules will be pushed into surface pores as concentration and osmotic pressure increases. In studies with porous glass, we have noted that when the pores in the substrate begin to approach the size of the probe molecule there is an apparent elastic response, even though the glass samples have a modulus well outside the range of this test. However, when zeolite with very small sub-nanometer pores is used no apparent elastic response is noted because the dextran cannot penetrate into such small pores.

The moduli of pulp fibers measured with the present technique are very low, in the range of 150–1500 Pa. The results previously reported for pulp fibers

are clearly higher. For example the axial tensile modulus of pure cellulose microfibrils in the wet state was reported to be 128 GPa [22]. For holocellulose fibers the wet axial modulus was found to be 9.2 GPa [23]. The transverse moduli of wet unbeaten softwood Kraft measured with atomic force microscopy micro-indentation gave value of 7 MPa [24]. While we tend to believe that the modulus of the outer surface of swollen pulp fibers, when viewed on a molecular level, is very low, it is apparent that the moduli calculated from the dextran measurements are at least partly confounded by surface porosity and other topographical considerations.

Scallan and Tigerström [25] proposed a method to calculate elastic modulus of water swollen cell wall. In this method, osmotic pressure is altered in the cell wall by changing the acid group counter ions from  $H^+$ -form to  $Na^+$ -form. Using the  $FSP_0$  in Table 1 and fiber charge of  $58 \pm 5$  and  $55 \pm 5$   $\mu\text{mol/g}$ , for pulp fibers and MFC, the moduli were calculated. The moduli for pulp fibers and MFC were determined to be 5.58 and 0.016 MPa, respectively. Despite the limitations of the techniques, both the dextran method and Scallan et. al earlier method indicate that MFC is a material with a very low modulus in the water swollen state.

The way in which fibrillar structure may relate to the measured inaccessible water and elastic modulus is shown graphically in Figure 4.

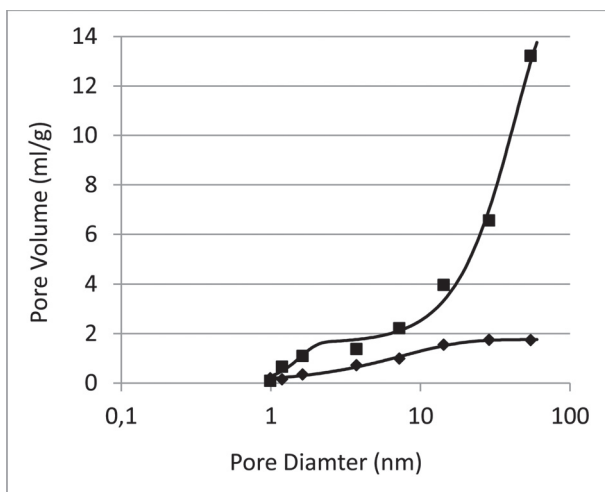


**Figure 4.** Schematic showing the swelling response of a fibrillated cellulose structure to external osmotic pressure exerted by a coiled dextran molecule. Osmotic pressure increases from a to b. In c the interstitial water within the MFC network structure is shown.

### **The pore size distribution of MFC with solute exclusion**

The goal of our work is to develop an understanding of the particle level swelling and pore structure of MFC. Therefore, it is necessary to eliminate the interparticle water effects that have complicated the above discussion. We have approached this problem by measuring the water inaccessible to probe molecules of varying size from 54 nm (2M Dalton) down to 1 nm (sucrose). This allows one to plot a pore size distribution (PSD) by assuming the probe molecule diameter is equal to the pore size. The difference compared to earlier solute exclusion experiments [12,13] is that in the current work the dextran sorption and osmotic effects are accounted for. Our hope in doing this exercise was that the interstitial spaces between the MFC were sufficiently large compared to the pores within the MFC body that we could detect two pore size distributions, which could then be resolved.

The results of this study are shown in Figure 5. The parent Kraft pulp fibers show a single PSD with a cumulative pore volume of 1.7 ml/g. It is known from earlier studies [26,27] that the pore size distribution of low yield pulp fibers is, in fact, the sum of two closely overlapping distributions. The spaces within the microfibril aggregates or within hemicellulose gel structures (micropores) can be detected with thermoporosimetry separately from the larger pores (macropores) formed by the dissolution of lignin between the lamellae. The distributions are so

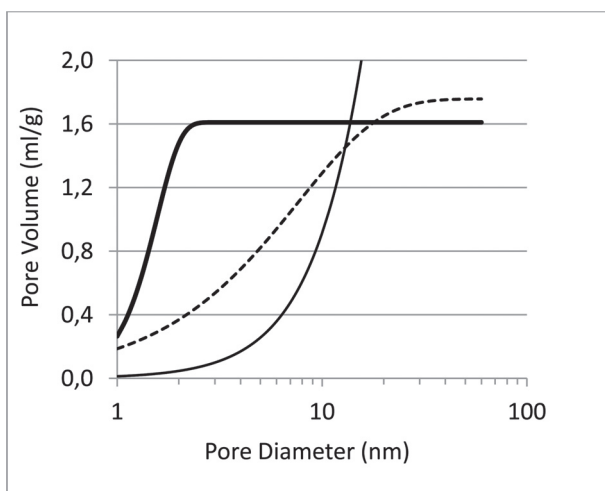


**Figure 5.** The cumulative pore size distribution of MFC (◆) and the parent Kraft fibers (■) measured with solute exclusion.

closely overlapping that these are not detected independently in a single solute exclusion experiment. However, for the MFC samples the PSD appears to be the sum of two separate distributions. The bimodal PSD arises because the pores within the MFC structure are much smaller than the interstitial pores between the particles.

To better illustrate the formation of a bimodal PSD when fibrils are liberated from the cell wall, the data in Figure 5 was fit with a single Weibull function for the pulp fibers and two Weibull functions for the MFC samples. The curves in Figure 5 appear to have reasonable agreement with the data. The MFC sample was then deconvoluted to form the separate distributions. The results are shown in Figure 6. From this exercise, the pore volume (particle level swelling) of the MFC sample was found to be 1.6 ml/g which is almost the same as the original pulp fibers (1.7 ml/g). The pores in the MFC sample range from below 1 nm to slightly less than 3 nm with an average of 1.4 nm. Pores between the MFC range from around 3 nm with an undefined maximum. The PSD of the pulp fibers is much broader than the MFC. For the pulp fibers, the pores range from below 1 nm to about 30 nm with an average pore diameter of 7.5 nm.

In Figure 6, it is apparent that the pore size distribution of the fibrils changes greatly when these are removed from the cell wall in MFC manufacture. The pore volume at a value of 3 nm can be taken as a measure of the fibril swelling because



**Figure 6.** The cumulative pore size distributions of the MFC and its parent fibers (dashed line) derived from the mathematical fit to the data shown in Figure 5. MFC has two distinct distributions, pores within the fibrils (heavy solid line) and pores between (solid light line).

the fibrils PSD reaches a plateau at this value. Within the cell wall the fibrils have a swelling around 0.5–0.6 ml/g, but in the form of MFC the swelling has increased to 1.6 ml/g. This suggests that the process of mechanical defibrillation involves loosening of the internal fibril aggregate structure on a very small length scale. This “nanoscale internal fibrillation” is analogous to the loosening of the cell wall structure in pulp refining. In that case, the internal fibrillation involves mainly loosening of bonds between the fibril aggregates as opposed to within the structure [21].

As a consequence of these experiments, we have noted that a good way to measure the fibril swelling for intact pulp fibers is simply to use a probe molecule around 3 nm big. In practice, we use a 6000 Dalton dextran probe with a diameter of 3.6 nm. The ability to measure fibril swelling independently from cell wall swelling (using the 2 M Dalton dextran) gives useful information on fiber ultrastructure in a range of applications.

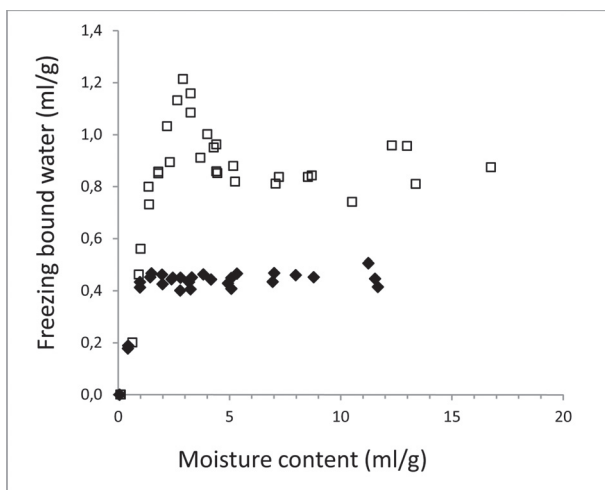
## **Thermoporosimetry**

### *Pore water*

Another way to garner information on the porous structure of MFC is to use thermoporosimetry. In earlier work [26] Maloney et al has developed a technique suitable for measuring the pore size distribution of wet pulp fibers and other cellulosic materials. The essential idea is that the water held with the small pores inside the cell wall has a depressed melting temperature. The amount of melting temperature depression can be related to the size of the pores via the Gibbs-Thomson equation. In addition to this fraction of “freezing bound water” (FBW), some of the water inside the cell wall does not freeze at all. This gives rise to a second fraction of “nonfreezing water” (NFW), which together with the FBW can be used to estimate the water inside the microreticular system. This is essentially the same as the water inside the fibril aggregates. Water inside the larger macropores in the cell wall does not display any anomalous freezing behavior.

The procedure used to measure FBW and NFW is described in more detail in the experimental section.

The FBW for the MFC and the parent pulp fibers is shown in Figure 7 in the moisture content range from bone dry to above 10 ml/g. For the pulp fibers, the FBW is a constant 0.4–0.5 ml/g until the sample dehydrates below 1 ml/g. The MFC, however, displays rather curious behavior. The FBW is constant over the range 15 to 5 ml/g, then increases to peak at about 3 ml/g and finally decreases to zero as the sample dehydrates. This seems to indicate that as the MFC dries out and the individual fibrils are pulled together by surface tension

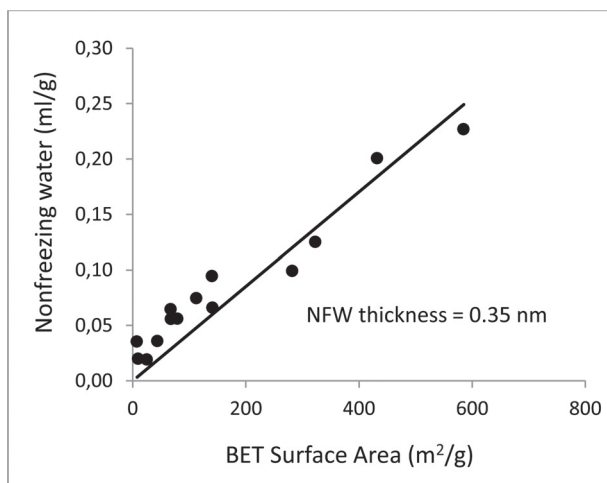


**Figure 7.** The freezing bound water (FBW) as a function of moisture content for MFC ( $\square$ ) and parent fibers ( $\blacklozenge$ ). The FBW is the water held in small pores which is still capable of freezing.

forces, the pores between the fibrils eventually come into the size range where they are capable of depressing the melting temperature of water and are thus included in the FBW measurement. Above a moisture content of 5 ml/g, the spaces between the fibrils are large enough that these do not contribute to the measurement. This “consolidation peak” appears to be a feature of nanocellulose (also oxidized fine nanocellulose shows this effect) that the authors have not observed in other cellulosic polymer or pulp fiber materials.

### *Nonfreezing water*

It has been widely noted [28–31] in hydrated biomacromolecule systems that some of the water does not freeze at all. While there may be several thermodynamic and kinetic factors that prevent freezing, the nonfreezing water (NFW) is generally used to indicate a type of bound or interfacial water. In any case, the quantity of NFW must be included together with the FBW in order to estimate the fibril swelling [32]. In order to get a better idea of how nonfreezing water relates to the hydrated surface area, the NFW vs. surface area for some porous classes was determined. The surface area of the porous glass samples was determined from an  $N_2$  adsorption experiment and application of the BET isotherm model. From the results shown in Figure 8, the NFW is directly proportional to



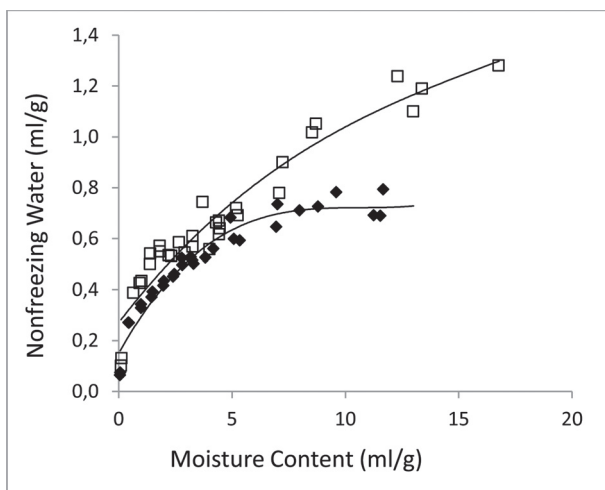
**Figure 8.** The nonfreezing water vs. BET surface area for a series of porous silica samples.

the surface area. The thickness of the NFW layer, calculated from the slope of the line, was determined to be 0.35 nm. This is very close to the diameter of a water molecule, which is 0.30 nm.

In this system, at least, the NFW is approximately 1 monolayer of water. This agrees with earlier work by Jähnert et. al [32]. This suggests that in water saturated polymer systems the amount of NFW may be used to measure the hydrated surface area. This could be extremely useful, because there are not many techniques that can measure surface area in the wet state for cellulosic and other gel-like materials. The hydrated surface area of such materials cannot be measured in the dry state because the structure collapses or is distorted when water is removed. Any techniques that attempt to prepare aerogels from hydrogels are always subject to artifacts that are introduced when the sample is prepared. The surface area of water swollen samples must be determined in the wet state.

The NFW for the MFC and the parent pulp fibers as a function of moisture content is shown in Figure 9. For the fibers, the NFW reaches a plateau value around 0.7 ml/g. This corresponds to a surface area of 2000 m²/g using the relationship shown in Figure 8. This is a fairly reasonable estimate of hydrated surface area, considering the water can penetrate the fibrils and access the outer surface of the elementary fibrils as well as amorphous regions of the cellulose.

For the MFC sample, the increase of NFW over the entire moisture content range is curious. One interpretation of the data is that the hydrated surface area in



**Figure 9.** The nonfreezing water for MFC (□) and the parent pulp fibers (◆) as a function of moisture content.

the MFC is significantly higher than for the pulp fibers (3500 compared to 2000 m<sup>2</sup>/g) and that the surface area collapses starting already at very high moisture contents. While this is possible, it does not seem very likely as we see no evidence of pore collapse at high moist contents in Figure 7. It is conceptually difficult to understand how removing water from the outside of the MFC can cause any reduction in a monolayer of bound water.

A second possibility relates to the way in which NFC is measured. While it is fairly certain that NFC exists, since at moisture contents below about 0.2–0.3 ml/g we do not observe any freezing transition, it is somewhat more ambiguous what happens at higher moisture contents. This is because the calculation of NFC assumes that the heat of fusion of water within the fibrils is the same as that of bulk water; 334 J/g. In our studies with porous glasses, we have found that lowered melting enthalpy is not a significant factor affect pore volume and have thus discounted this effect. However, for NFW measurements, especially at higher moisture contents, this factor may be important. Because the MFC sample has more water in small pores than the pulp fibers it is entirely possible that the freezing water in the MFC sample also has a lower heat of fusion. Such behavior could explain the apparently higher NFW and the shape of the NFW curve for the MFC sample.

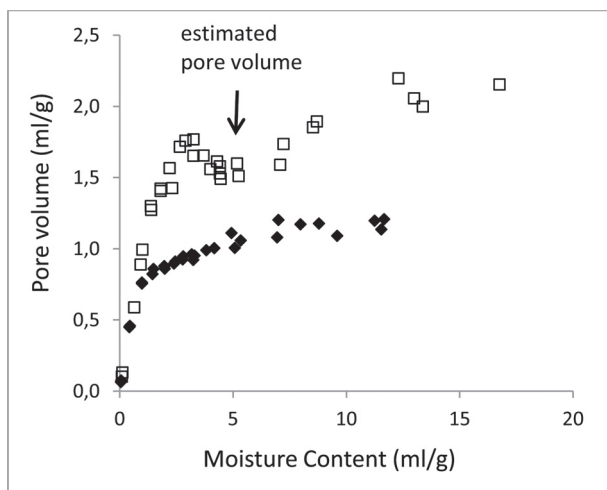
The possibility to use NFW to probe hydrated surface area is indeed intriguing. However, a more thorough description of the factors affecting water freezing and its measurement in cellulosic materials is still needed.



*Total pore volume by thermoporosimetry*

The total pore volume from thermoporosimetry includes the sum of NFW and the FBW. This is shown in Figure 10. The fibers reach a plateau value around 1.1 ml/g, which compares to 1.7 ml/g FSP<sub>0</sub>. So in that case 0.6 ml/g of water is held in the cell wall in macropores. The MFC curve in Figure 10 displays complex behavior due to the consolidation peak in Figure 7 and possible artifacts in the NFW at higher moisture contents. In this case, we believe that the best estimate of pore volume for the MFC is taken at the moisture content just above the consolidation peak; 5–6 ml/g. At higher moisture contents the NFW value loses precision and is highly affected to any distortions to the melting enthalpy. In the moisture content range 5–6 ml/g the pore volume for MFC is about 1.6 ml/g – in excellent agreement with the solute exclusion results.

Clearly, the agreement between solute excellent and thermoporosimetry cannot be considered perfect, because each method suffers from its own drawbacks and complicating factors. The solute exclusion method does not take into account all the factors that can influence the interaction of a probe molecule with a porous system (such as the probe poly-dispersity), but it does take into account two important factors; dextran sorption and external osmotic pressure. So it is a step forward in the right direction. The thermoporosimetry technique suffers from



**Figure 10.** The pore volume for MFC (□) and the parent Kraft fibers (◆) as a function of moisture content. The arrow shows our best estimate of pore volume in the water saturated state – about 1.6 ml/g.

various complicating factors at play over the range of moisture content from dry to dilute state. Despite these issues, both techniques agree reasonably well and are suitable for characterizing swelling and pore structure of MFC.

## CONCLUSIONS

The classical solute exclusion technique was further developed by taking into account the small adsorption of dextran onto the cellulose surface and the osmotic pressure exerted by the dextran probe on the swollen surface. The model that was developed fit the observed data well. By varying dextran concentration, and applying the model it was possible to extract two parameters of interest; the  $FSP_0$  describes the swelling at 0 external osmotic pressure while the isotropic modulus,  $E_i$ , gives a measure of the softness of the external cellulose surface in the water swollen state.  $FSP_0$  was found to give reasonable values for several different fibers tested.  $E_i$  is low compared to other methods for measuring cellulose modulus. This is partially explained by intrusion of the dextran probes into surface pores.

The new solute exclusion technique was applied to a sample of MFC and the Kraft fibers from which it was produced. The resulting bimodal distribution was resolved to show that the particle level swelling of MFC was 1.6 ml/g, which is about the same as the parent fiber (1.7 ml/g). However, when the fibrils are liberated from the cell wall in grinding the swelling increases from about 0.5–0.6 ml/g to the MFC state of 1.6 ml/g. This shows that the internal pore structure of fibril aggregates is severely disrupted when these are removed from the cell wall in grinding.

The thermoporosimetric analysis of the MFC showed interesting behavior. The freezing water in pores was found to be constant in the fully saturated state but then increase prior to final dehydration. This is believed to be related to the consolidation of the fibril aggregates as a film is formed. The nonfreezing water was found to be approximately a monolayer on silica samples, suggesting that NFW could be used to measure hydrate surface area in cellulosic samples. This analysis gave an estimate of 2000 m<sup>2</sup>/g in pulp fibers. For MFC, the NFW varies over a wide moisture content range. The best estimate of pore volume from thermoporosimetry at moisture content of 5–6 ml/g was 1.6 ml/g for MFC; in agreement with solute exclusion results.

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## Transcription of Discussion

# THE SWELLING AND PORE STRUCTURE OF MICROFIBRILLATED CELLULOSE

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*Lars Wågberg*      KTH

Thank very much for your presentation. I have a couple of questions. The first is, how do you know that the dextran is adsorbing? How do you determine that?

*Thad Maloney*

It should be determined independently, which I have not done. The only evidence I have, is that you will get negative fibre saturation points if you don't account for the adsorption. These results are not sensible. Fibres adsorb dextran a little, for the MFC, the adsorption is much higher. I was really disturbed by that, and because I talked to Per Stenius when I started suspecting the adsorption of dextran and he said that dextran is too soluble to adsorb. It may be very weak adsorption, more of an association with the surface and you could wash it away, no doubt. But the way I make my measurements is I mix up the dextran in the material in a centrifuge tube, then I centrifuge it and I extract the supernatant from that. The adsorption should, however, be confirmed independently.

*Lars Wågberg*

We can measure it together with some of the techniques that we have. The second question I have is due to the fact that I am a bit bewildered: you say that the fibrils

## *Discussion*

and the fibres have the same pore volume from solute exclusion with values at 1.6 to 1.5 mL g<sup>-1</sup>. How do you look upon the structure of the fibre wall, before it is disintegrated? Furthermore, the water, where is it?

*Thad Maloney*

It has the same pore volume actually, so I mean the fibre saturation point for the fibre was 1.8 mL g<sup>-1</sup>, and for the fibrils it turned out to be 1.6 mL g<sup>-1</sup>, but their pore size is completely different. In the fibres you have pores that range from 0 to 30 nm, I believe, and that's what I wrote my doctoral thesis on, that there are two overlapping distributions that you cannot resolve with this technique. You have water in the fibrils and you have a water in the macropores which are formed by the dissolution of lignin in the chemical pulping process. That's where I think the water is in the fibres, but in the fibrils it is obviously very different. Fibrils have a very much tighter pore size distribution.

*Lars Wågberg*

I am astonished that FSPs for fibres and MFC end up at the same level. Do you have an explanation for that?

*Thad Maloney*

I do not know why they have ended up on the same level, but I believe it. I have results also from thermoporosimetry. We have two imperfect methods which agree.

*Gil Garnier*      Monash University

I have a question about non-freezing water: do we observe the concept of non-freezing water in other materials such as activated carbon, cyclodextran, starch? Can you comment and is it different from cellulose?

*Thad Maloney*

As far as I know, at least, it is a universal property of hydrated materials, so hydrophobic materials, and hydrophilic materials, glasses, inorganic, organic materials show non-freezing water and it is not just an anomaly based on enthalpy measurements. You can do experiments for example with NMR and freeze the sample and then measure directly relaxation properties of the water, or dielectric spectroscopy and similar techniques can be used. So the non-freezing water really

exists, and it exists in all kinds of materials and there is, I would say, no universal understanding of it or really excellent theories to explain what it is. As I said, there are kinetic theories and thermodynamic theories that try to explain non-freezing water. The kinetic theories say that in fact water is freezing very slowly: if a sample is kept frozen for a million years, it would freeze. I have tried, actually, not for a million years but for long periods of time, but could not find an effect. So, in this case, I am trying to relate the non-freezing water to the surface area, to the hydrated surface area. Many other papers will relate non-freezing water to certain chemical structures, site adsorption theories and things like that. In fact, there may be really multiple reasons why water does not freeze depending on the system. So it does make it a little bit difficult to interpret non-freezing water data.

*Wolfgang Bauer*      Graz University of Technology (from the chair)

Would it be interesting to use that procedure also on the TOCN fibres that Professor Isogai presented?

*Thad Maloney*

Absolutely and I have started doing that. I have not looked at a whole lot of samples with the thermoporosimetry, but I have started looking at TEMPO samples in different ionic forms and so on. At least for the samples I have, I am getting a value of 4 to 5 mL g<sup>-1</sup> of water. We have to also keep in mind that what I am saying is applicable to particle level swelling, the water inside a particle. What actually happens, if my particle starts approaching molecular dimensions, and if I go all the way go down to CMC, how much water is in a CMC molecule? I think not really anything, it is bound on the surface. So the idea of particle swelling starts to not apply. I think for TEMPO NFC you start to have the same thing. As you go to closer to molecular dimensions, it is more and more difficult to apply these techniques. Certainly, for solute exclusion techniques, the MFC is absolutely the limit of its applicability. If we would go to even fine MFC grades, it is very difficult to do, and for TEMPO NFC grades it is impossible. So for that reason, I have focused more on the thermoporosimetry.

*Asaf Oko*      SP Technical Research Institute of Sweden

Perhaps you have said something about it: do you think the junctions between fibres, and especially between nanofibrillated cellulose fibrils, are dominant in the water absorption or it is not really important? So when you prepare your samples, do you make sure that all the fibrils are totally separated or you do not really care about it? Do you want to go for realistic values where you have flocs?

## *Discussion*

*Thad Maloney*

I think it is very important. The fibrillation and the floc structure is important, and mixing in sample preparation is everything, you have to care about that. I have an easy case because I have a sample and it is like it is. We prepare it as carefully as we can and homogenise the material, mix it carefully and try to control all aspects of that. But definitely, depending on the flocculated structure and the history of the sample, it affects the results. In this way this material is much more difficult to work with than pulp fibres.