Effect of Fiber Wall Pore Structure on Pulp Sheet Density of Softwood Kraft Pulp Fibers

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In this study fiber cell wall porosity was altered by fiber line simulation in a laboratory. The changes in the fiber cell porosity were analyzed with a water retention value (WRV) test. Pore size distributions were measured by differential scanning calorimetry (DCS), and atomic force microscopy (AFM) was used to determine the cell wall pore area from cross sections of the S2 layer of the cell wall. WRV was shown to correlate with the amount of water in the pores with a diameter of at least 200 nm. Changes in the non-freezing and total bound water did not affect the WRV. The calculated shrinkage forces generated by the capillary forces in different pore cell wall structures correlated with the sheet densities generated by fiber networks. It was observed that the swelling of the cell wall, defined as an increase in the diameter of the cell wall, was most likely not occurring or was very difficult to detect.

Keywords: Pulping; Kraft fiber; Softwood; Cell wall; Pores; Sheet density

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INTRODUCTION

The production of raw materials with uniform, suitable, and predictable properties is very important in order to increase competitiveness in the pulp and paper industry. For many paper products, chemical softwood and hardwood pulps are the most expensive component. The papermaking potential of the chemical pulps is generally evaluated after refining the pulp fibers and measuring, for instance, pulp sheet properties such as tensile, tear, bonding strength, and pulp sheet bulk. Other pulp properties of interest are fiber dimensions (fiber length, fiber wall thickness, *etc*.), chemical composition, and fibers' ability to swell and form inter-fiber bonds.

A property that has a significant economic impact on the production of paper products is the density of the pulp sheet. Density or bulk is affected by both the properties of the raw materials and the production process. The bulk of fibers affects the amount of fibers that are needed for a product, which has direct impact on production cost. Therefore the relationship between pulp fiber and paper properties has been extensively studied (Dadswell and Watson 1962; Dinwoodie 1966; Wardrop 1969; Scurfield 1976; Lindström 1980; Amidon 1981). Not surprisingly, thick-walled fibers have been shown to form bulky sheets (less fiber flexibility) of low tensile, but high tearing strength (Maloney 2000; Lindström 1980). Papermakers typically want their paper to have high bulk, while still meeting strength requirements. High bulk results in easier dewatering because of the porous structure of the sheet, therefore enabling water to exit easily. Good bonding ability and high network activation results in a higher tensile strength.

Other factors affecting pulp sheet bulk, such as fiber cell wall swelling, has received much attention in this particular area of research. Several different methods have been used in the research, such as microscopical examination, the water retention value method (WRV), the fiber saturation point method (FSP), and the differential scanning calorimetry method (DSC) for determining swelling of the cell wall.

Microscopical examinations of the shrinkage/swelling behaviour of pulp fibers and kraft handsheets have been studied, for example, by Weise (1997), Enomae and Lepoutre (1998), and Moss and Pere (2006). Sisson (1943) reported that fibers swell under the influence of water at their amorphous regions. Lindström (1980) showed that fibers typically do not swell in their width; rather, swelling causes an increase in the fiber wall thickness in the direction of the fiber lumen (Lindström and Carlsson 1982).

Jayme (1958) reported that WRV, fibers ability to hold water in the cell wall, and flexibility have been found to decrease with increasing mean fiber wall thickness, which is probably due to the water retained by capillarity inside the lumens. Water retention value (WRV) and fiber flexibility are manifested as cell wall swelling (Lindström 1980; Lindström and Carlsson 1982).

WRV has also been found to correlate with the fiber saturation point (FSP). FSP is a solute exclusion test and measures the water in the fiber wall that is inaccessible to a probe polymer.

Maloney (1998) presented results of the DSC method for determining the amount of water in the cell wall and thus the swelling of the cell wall. The DSC method is based on measuring water absorbed in pulp fibers, which melts at depressed temperature, as a manifestation of freezing bound water. The method involves melting the water isothermally at incremental temperatures approaching 0 ^{o}C, and the results permit calculation of cell wall pore size distribution (Maloney 1998).

Because the bulk of the pulp sheet is important for the papermaker, a detailed understanding of how the fiber cell wall pore structure changes in the pulp production is necessary for pulp properties development. It has been reported that during industrial digester operations (Joutsimo 2004), major changes in the pulp properties, *e.g.* in fiber cell wall swelling, can be observed. In the industrial continuous digester operations, wood chips undergo mechanical treatment during impregnation and cooking. This happens, for example, in chip feeding with a pump or screw to an impregnation vessel. The impregnated or partially delignified chips are discharged from an impregnation vessel with a rotating bottom scraper. Transfer circulation, digester top and bottom are equipped with pumps, screws, or scrapers, which apply force to delignified wood chips. In the fiber line, tanks are equipped with mixers, and pulp is moved with pumps, which all apply forces to fibers.

In this article, we first present the experimental arrangements for the simulation of pulp mill fiber line, analysis of chemical composition of the pulp, and paper technical properties of the pulp. We then present determination of water retention value (WRV), methods of differential scanning calorimetry (DSC), and atomic force microscopy (AFM). Next, we report results regarding changes in the cell wall structure and effects on pulp sheet density. Finally, structural differences of the cell wall affecting the shrinkage of the fiber and the bulk of the fiber sheet are discussed.

EXPERIMENTAL

Raw Material and Cooking Experiments

Scots pine (*Pinus sylvestris*) was used as the raw material in this study. Two types of industrial chips were used: normal roundwood chips (RW) and sawmill chips (SC). These chip types were chosen to give a wide range of fiber dimensions. The chips were stored fresh and were not screened in the laboratory.

The cooking experiments were performed in two different types of digesters. The reference pulps were produced in a 30 L forced circulation laboratory digester, whereas the simulated fiber line pulps were cooked in a laboratory digester equipped with a mixer. The cooking conditions were the same in both cooking experiments. The cooking liquor was prepared in the laboratory from NaOH and Na_2S of industrial grade. Deionized water was used in all experimental steps. The liquor to wood ratio was 4/1 in all cooking experiments. The effective alkali charge in each cook was 4.5 mol NaOH/kg dry wood. The sulfidity used in all cooks was 35%.

The following temperature profile was used in all experiments: heating from room temperature to 80 ^{o}C in 30 min; heating from 80 ^{o}C to 170 ^{o}C in 90 min; cooking at 170 ^{o}C for 2 h. In the cooking experiments carried out in the forced circulation digester, the amount of wood was 4.5 kg, calculated as oven-dry. The amount of wood used in the reactor equipped with the mixer was 2.5 kg dry wood. The pulps cooked in the digester with the mixer were stirred throughout the cook at 30 rpm in order to ensure even alkali and temperature distributions. Mixing at 170 ^{o}C started 15 min before the end of the cook and was carried out at a speed of 350 rpm. The total amount of energy fed into the system during mixing was approximately 10 kWh/t. These fiber-line simulated (mechanically treated) pulps in this study are referred to as treated (T). After cooking, the pulps were washed and screened.

In the washing and screening, special care was taken in order to avoid fines losses *e.g.* in washing, fabrics were used, which retain fines with the pulp. After cooking, the chips were disintegrated in a Wenberg type disintegrator. Pulp was washed in a screen basket, and outgoing washing filtrate was directed through a wire fabric, which has mesh size of 70. The retained fines in the fabric were returned to the pulp. Cooking trials were carried out by VTT.

Pulp Properties Analysis and Refining

Pulps were refined using a PFI mill, and the sheets for testing were made according to ISO 5269-1 from pulps without fines removal. Kappa number was determined according to ISO 302 and viscosities according to ISO 5351. Fiber length, fiber coarseness, and fines contents were measured using a Kajaani FS-200 device. Kajaani FiberLab equipment was used to measure cell wall thickness, fiber cell wall diameter, and fines content from the pulp samples.

Beating was performed using a PFI beater according to EN ISO 5264-2 at 500, 1000, 1500, and 2000 revolutions. Elastic modulus was measured according to EN ISO 1924-2. The apparent bulk density was measured according to ISO 5270.

The water retention value (WRV) was measured according to ISO/FDIS 23714. The hemicelluloses composition was measured *via* acid methanolysis (Laine *et al.* 2002).

Thermoporosimetry Analyses

One gram of the washed unbleached fibers was washed thoroughly with distilled water to remove dissolved substances. The acid groups in the cell wall were exchanged to the Na form by heating a 1% slurry of the pulp in 0.1 M sodium acetate for 1 h at 40 ^{o}C. The pulp was then rewashed several times with distilled water and centrifuged at 3000 g for 10 min to adjust the moisture ratio close to the fiber saturation point. After centrifuging, 2 to 2.5 mg of wet pulp was sealed in an aluminum sample pan. The amount of freezing and non-freezing water was determined using thermoporosimetry. A Mettler 821 differential scanning calorimeter (DSC) was used for thermoporosimetry measurements, and they were performed according to Maloney (1998) and Maloney and Paulapuro (2001). The isothermal melting set points used in this study were -8, -5, -3, -2, -1, -0.6, -0.4, and -0.2 ^{o}C. Final temperature corresponds to maximum pore diameter of 216 nm. The measurements were done at Helsinki University of Technology, Aalto (Finland).

Atomic Force Microscopy Pore Area Measurement

Never-dried unbleached fibers were rapidly frozen in liquid nitrogen, freeze-dried for 24 h, embedded in epoxy-resin (TAAB 812), and hardened at 70 ºC for 24 h. The pulp fibers were then oriented along the fiber axis before they were impregnated with melted PEG under vacuum at 70 ºC for 24 h. After impregnation, the fiber surfaces were rapidly rinsed with deionized water in order to remove PEG from the actual fiber surfaces. Samples were then embedded in an epoxy-resin (Spurr from analytical standards) that was hardened for 8 h in 70 ºC. The embedded fibers were then cut perpendicular to the fiber direction into 0.5 μm thick cross sections using a rotary micro-tome (Leica Jung RM 2065).

Fiber Cross sections were examined with an AFM device using TappingMode™. A NanoScope® IIIa Dimension™ 3000 with sharp tapping mode probes was used. The specimens were scanned using a tip with a radius about 10 nm. The length of the cantilever was 125 μm, the force constant was 42 N/m, and the resonant frequency was 320 kHz. The samples were scanned at ambient temperature and humidity. Images were taken in both height mode, in which the deflection of the cantilever is directly used to measure the z position, and in phase mode, where the phase lag of the cantilever is used to determine differences in material stiffness.

An image processing software (called IMP), developed at the Center for Image Analysis in Uppsala and based on the watershed algorithm, was used for evaluation of the AFM images (Nordin 1997; Wählby *et al.* 2002). After detection by the software, each individual aggregate area was calculated in pixels, which then was transformed to nm. From the mean area values of the aggregates their widths can be calculated, assuming a square cross-section for the cellulose aggregates. The shape of the tip influences the apparent width and height of the cell wall features, with low areas appearing smaller and high features appearing larger. The enlargement of the AFM probe is hard to calculate with high accuracy because several factors are involved in the result, factors such as the tip radius, the radius of the features imaged, and the depth of the valleys between individual objects. A rough estimate of the enlargement effect is however possible. The enlargement effect was estimated (Fahlen 2005) by knowing the angle of the tip (10°) and an average value for individual cellulose aggregate height from the AFM software's roughness function, and using ordinary triangle trigonometry.

RESULTS AND DISCUSSION

Pulp sheet densities, hemicellulose content, composition, and fiber morphology were investigated from the unbleached fibers. Then WRV, DSC, and AFM results were used to analyze cell wall structure and degree of cell wall swelling. Finally the effect of different pore size distributions and cell wall structure on shrinkage strain of porous material, *i.e*. the pulp sheet density, is discussed.

Cooking Hemicellulose Composition and Pulp Sheet Density

The wood raw material was cooked to kappa level approximately of 28. From the unbleached pulp, samples were measured for cooking yield, kappa number, viscosities, and fines contents, which are presented in Table 1.

Table 1. Pulp Characteristics after Cooking of the Pine Pulps

Raw material	Yield, % total	Kappa number	Viscosity, ml/g	Residual alkali, g/l	Viscosity at kappa 28, ml/g	Fines, % Kajaani FS-200	Fines, % Kajaani FiberLab
Pine RW	50.4	29.5	1220	3.5	1200	3.01	2.71
Pine RWT	46.9	26.3	1150	3.9	1175	3.08	2.98
Pine SC	49.1	27.6	1320	4.0	1325	2.94	2.46
Pine SCT	48.6	26.3	1200	3.7	1225	2.92	3.05
RW = round wood, SC = saw mill chips, T = treated							

Results in Table 1 show that there were small differences in kappa numbers between the raw materials. The average kappa number was 27.5 and kappa numbers of all pulps were in the range of +/- 2 units. The residual alkali after cooking was also similar for the treated and untreated pulps. The dry content measurement was not very exact because the pulps were not spin-dried. The yield determination, therefore, was not very reliable. If compared at the same kappa number, the differences in viscosity between the untreated and treated pulps from the same raw material were moderate. What was clear, however, was that treated pulps had slightly lower viscosities. Fines contents of the pulps remained approximately at the same level; however Kajaani FiberLab seemed to give a slight increase in fines content of the treated pulps. Despite the measures that had been taken in order to avoid fines losses, it could be possible that some fines were lost during washing. However, it can be assumed that all the pulps had similar amounts of fines.

An increase in the hemicelluloses content and composition (*e.g*. increase in xylan content) of the fiber is generally thought to affect sheet density. This has been explained by the ability of hemicelluloses to retain more water; thus fibers with more hemicelluloses are able to retain more water in the fiber cell wall pores. Higher amounts of water in the cell wall has been reported to increase wet fiber flexibility, which by increasing fiber conformability increases pulp sheet density (Abitz and Luner 1991). Hemicelluloses content and composition was measured with acid methanolysis, and the results are presented in Table 2.

It can be seen from Table 2 that the total amount of hemicelluloses extracted by acid methanolysis was similar for all of the pulps. Contents of the different hemicelluloses in the pulp samples differed only in the Pine SCT sample, which showed somewhat lower xylose and mannose content compared to other samples.

Table 2. Hemicelluloses Content and Composition of Treated and Untreated Pulps

Sample, mg/100mg	Pine RW	Pine RWT	Pine SC	Pine SCT
Arabinose	0.76	1.1	0.74	0.78
Rhamnose	<0.1	<0.1	<0.1	<0.1
Xylose	5.3	5.2	5.2	4.6
4-O-methyl glucuronic acid	<0.1	<0.1	<0.1	<0.1
Mannose	2.8	2.6	3.0	2.4
Galactose	0.39	0.46	0.44	0.39
Galactoglucuronic acid	<0.1	<0.1	<0.1	<0.1
Glucose	4.2	3.4	3.7	3.5
Glucuronic acis	<0.1	<0.1	<0.1	<0.1
Total mg/100mg	13	13	13	12

The pulp sheet density as a function of PFI revolutions is presented in Fig. 1.

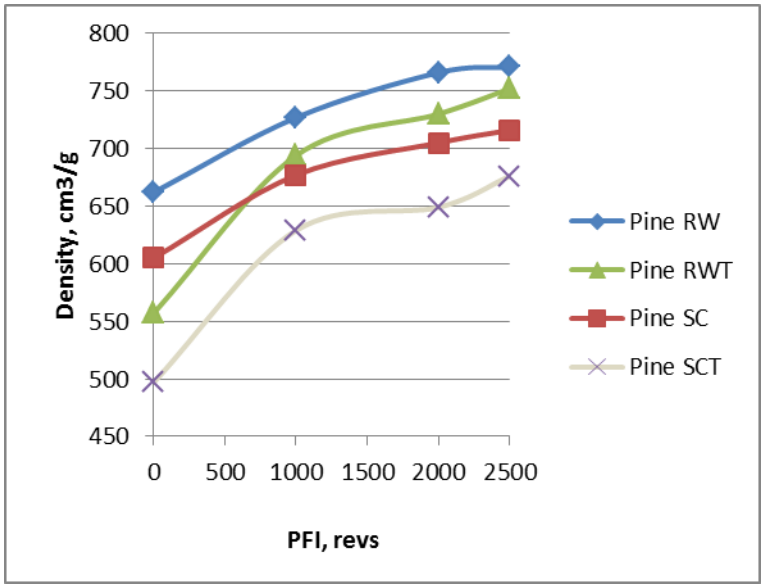

Fig. 1. Pulp sheet density as a function of PFI refining revolutions

Figure 1 shows that pine round wood fibers generated a denser sheet compared to pulp sheets made from pine saw mill chip fibers. The mechanical treatment decreased the sheet density of the pulp sheets made from both pine raw materials. The decrease in pulp sheet density was slightly higher for pulp sheet made from saw mill chip fibers. Based on the results in Table 2 it can be concluded that the small differences in hemicelluloses content or composition of the pulps cannot explain the differences in the sheet density results presented in Fig. 1.

However, a plausible explanation for decreased pulp sheet density of the treated fibers could be related to the loss of fines during pulp washing. Fines have a much larger specific surface area or surface area per unit mass than fibers. They are more swollen as well. In fact, fines carry nearly twice the amount of water per unit dry mass than fibers (Seth 2003; Luukko 1995). Because of their small size, large specific surface area, and

higher swelling, fines affect paper sheet structure and properties in several ways. Fines fill interfiber spaces during sheet dewatering. They increase sheet wetness for given dewatering conditions. Fines increase fiber-fiber interaction by increasing the fiber water-air interfaces where the surface tension force acts during sheet drying. Fines increase the shrinkage forces during sheet drying. Being hemicellulose-rich, fines probably improve fiber-fiber bond strength as well, particularly the sheet structure (Paavilainen 1990; Retulainen *et al.* 1993; Seth 2003). Seth (2003) has shown that by increasing fines content in the sheet consolidation increases significantly.

In the laboratory pulp sheet preparation, wet-pressing time was kept constant; therefore sheets with higher fines content would need higher dwell time (pressing time) in order to reach the same dry matter content. In our case if untreated pulps have higher fines content (if fines would be lost in washing of the treated fibers), then they would also have higher drainage time in the wire and in wet pressing. Therefore, those pulps sheets having lower fines content would also have lower moisture after wet pressing. High amount of fines in pulp sheet increases moisture in the sheet after wet pressing and therefore yields higher drying stresses during drying. Higher drying stresses increase the pulp sheet density (Patterson and Iwamasa 1999).

Another mechanism that could explain the decreased sheet density is the effect of fines losses on sheet forming and vacuum generation during drainage. If the fines of the treated pulps are lost either before or during sheet formation, this might result in a lack of choking or sealing effects; in other words, fines are not blocking the flow channels in the sheet during its formation (Hubbe 2002, 2007); thus vacuum dewatering elements on the paper machine are less effective in compressing the sheet during forming, leaving it with higher porosity. Lack of drainage resistance obviously leads to faster drainage time. Another theory similar to the choking effect, which could play a role, as presented by Sampson and Kropholler (1995), proposes that if fibers are able to slide past each other during the forming process, they tend to form a relatively dense mat. If they tend to stick together and not slide past each other, then one could expect a lower density sheet. In our case it could be hypothesized that fiber having a history of simulated mechanical fiber line effects on the fiber cell wall are stiffer and may have a higher degree of surface fibrillation which increases fiber entanglement and thus decreases sheet density. However, in earlier microscopy research (Joutsimo 2004), fiber surface fibrillation analysis was not able to detect differences in the fibrillation of treated and untreated fibers. Also, Zeng *et al.* (2013) reported similar results to ours; after treating bleached pulp mechanically at 170 ^{o}C, the pulp sheet density decreased from ~510 to ~470 kg/m^3 while fines content increased from ~6 to ~9%.

Fiber Morphology and Fiber Curl

Other factors that are generally thought to affect sheet density are the curl of the fibers (Seth *et al.* 1993) and fiber morphology. In Fig. 2, the fiber length and fiber curl as a function of PFI refining energy are presented. From Fig. 2a it can be seen that the fiber length of the treated fibers was slightly lower, especially with pulp cooked from sawmill chips. The difference was generated by the fiber curl, which, as can be seen from Fig. 2b, decreased for the treated fibers as a function of refining energy. However, it must be noted that the fiber curl of the untreated fibers increased slightly as a function of the amount of refining. This indicated that the fiber form did not have a significant effect on the fiber length, especially with pine round wood pulps. Also, it has been shown that the

fiber curl does not affect the sheet density (Robertsén and Joutsimo 2005). It must also be noted that the fiber curl of the untreated fibers increased slightly as a function of refining (Fig. 2b) when the sheet density increased (Fig. 1). Therefore, it is unlikely that fiber curl affects the sheet density. The fiber coarseness of the pulps is presented in Fig. 3.

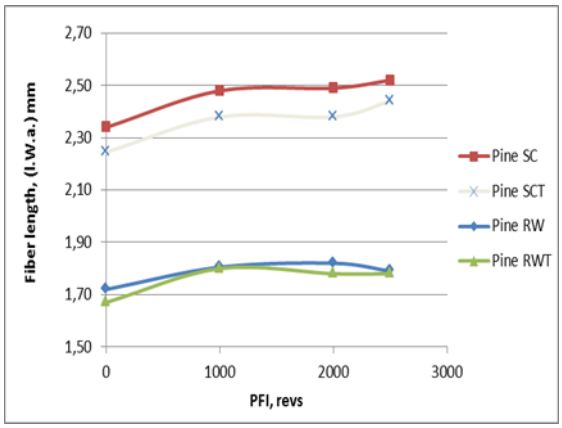

Fig. 2a. Fiber length as a function of PFI refining revolutions

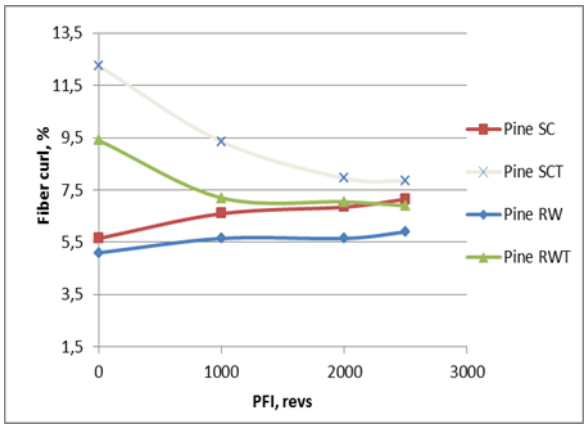

Fig. 2b. Fiber curl as a function of PFI refining revolutions

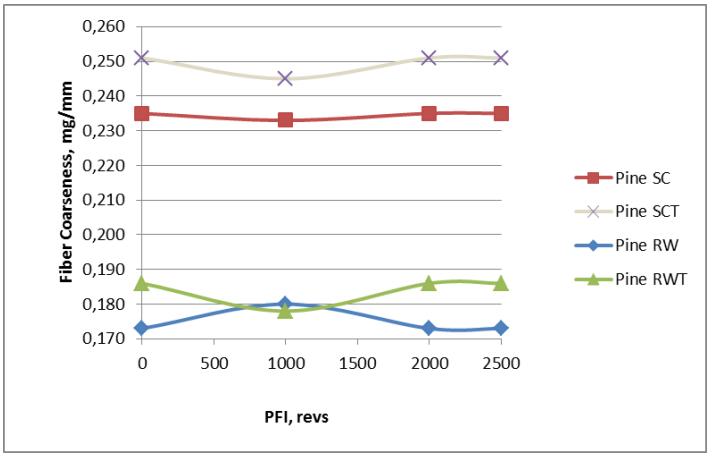

Fig. 3. Fiber coarseness of the treated and untreated pulps, measured by FS-200

Figure 3 shows that mechanical treatment seemed to increase the fiber coarseness. Coarser fibers are generally thought to give lower pulp sheet densities. High fiber coarseness is thought to decrease fiber flexibility, and therefore fibers in the sheet would not be conformable and would form a sheet with low density (Lindström 1980; Paavilainen 1990; Maloney 2000). In our results the increase in fiber coarseness can be explained by the decrease in fiber length. It seems that FS-200 cannot accurately determine fiber length when the fibers are curled or have kinks. It has been reported (Rauvanto 2010; Gärd 2002; Robertsén and Joutsimo 2005) that FS-200 and other fiber analyzers give lower or inconsistent length weighted fiber lengths when fiber curl or number of kinks is increased, while fines content is reported to be approximately at the same level. Therefore it can be considered that increased fiber coarseness is artificial due to measurement issues. Also Guy (2005) reports standard deviation for FS-200 coarseness measurements to be ± 0.012 mg/mm. This would mean that most

measurement points are within the deviation. However it can also be considered that some fines are not accounted for in the fines measurement and the fiber length has decreased, generating a higher amount of fines, despite the fact that the measurement shows higher fiber coarseness. It has to be noted, that in earlier work (Joutsimo 2004), after applying the same treatment to softwood fibers, no increase in fines content in the pulps could be detected with optical fiber analyzers or with DDJ (Dynamic Drainage Jar) measurements.

Fiber Swelling and Cell Wall

The fiber cell wall thickness and diameter were measured with the Kajaani Fiber Lab from unrefined fibers. The water retention value was also measured from unrefined fibers and is plotted together with the cell wall thickness (CWT) and cell wall diameter in Fig. 4.

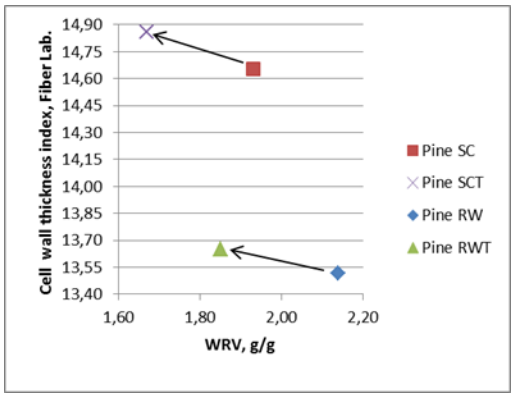

Fig. 4a. The CWT as a function of WRV for pulp samples

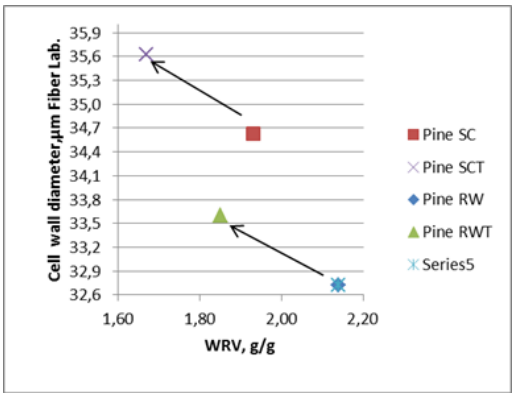

Fig. 4b. Cell wall diameter as a function of WRV for the pulp samples

Interestingly, Figs. 4a and 4b show that when the fibers were treated, the cell wall thickness index and cell wall diameter slightly increased (CWT approximately 1% and cell wall diameter increased 2.5%), while the WRV decreased by approximately 14%. Another aspect, which has to be taken into consideration, is that FiberLab cell wall measurement accuracy is 1.5 µm, meaning that measured increases of cell wall thickness or fiber diameter fall between the detection limits of the measurement. Gärd (2002) has also reported a slight increase in the fiber cell wall thickness due to different mechanical treatments of softwood pulp.

The above shown decrease in WRV is in line with results reported *e.g.* by Pulkkinen (2010), that when cell wall thickness increases, WRV decreases. However the magnitude of decrease in WRV in this study is much larger compared to values reported by Pulkkinen *et al.* (2008). It is possible that some fines would be lost in pulp washing, but it is rather challenging to attribute the detected decrease in WRV solely to the loss of fines, *e.g.* in pulp washing. The detected amounts of fines were approximately the same or slightly higher in the treated pulps, as shown in Table 1. If fines would have been lost, that would mean a significant cooking yield loss. In the case of Pine RW samples, WRV decreased from 2.15 g/g to 1.85 g/g. Considering that fines have WRV of 2.6 g/g (Luukko 1999) and fibers 1.85 g/g means, then in grams of pulp there would be 60% of fibers and 40% fines in order for WRV to be 2.15 g/g. The decrease in the amount of fines should have been approximately from 40% to 3%. Cooking yield should have

decreased in the same proportion, which we did not detect. Earlier studies have shown even larger decreases in WRV (from 1.95 g/g to 1.25 g/g) for spruce fibers as a consequence of a similar mechanical treatment. In this research the decrease in the water holding ability of the cell wall was ascribed to the structural change of the cell, thus opening of pores in the cell wall (Joutsimo 2004). Based on the discussion above, one could consider that the WRV probably does not describe the swelling of the cell wall. WRV is measured by centrifuging pulp fibers under constant g-force. It is thought that the slight change in the CWT indicates an increase in size of the pores in the cell wall. If this is the case, larger pores (due to lower capillary pressure) might not be able to hold water inside the cell wall when centrifuged at constant g-force and water might come out easier. Joutsimo (2004) reported that treated cell walls compared to untreated cell walls show higher accessibility in Simmons stain analysis, which is in line with the CWT result. Both the swelling or the lack of it and increase in the cell wall thickness should have an impact on the sheet density. The WRV development as a function of PFI revolutions for the samples is presented in Fig. 5.

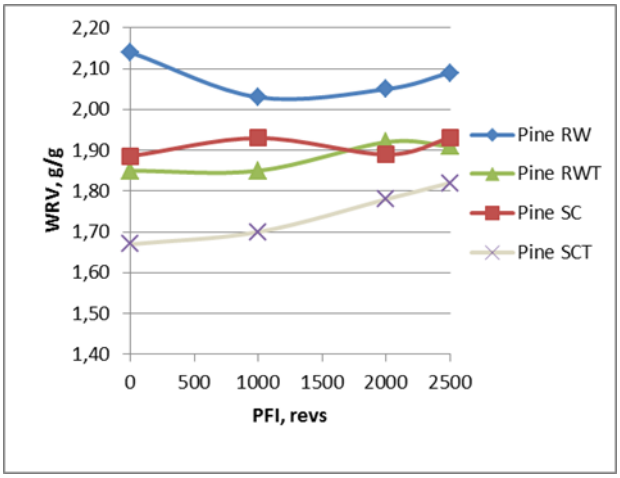

Fig. 5. WRV as a function of PFI for pulp samples

From Figs. 5 and 1, it can be obtained that when the difference in WRV between the treated and untreated pulps decreases, the difference in density also decreases. However, the difference in sheet density (20%, from Fig. 1.) measured from dried pulp sheets, in the beginning of the refining curve cannot be explained only by the difference in cell wall thickness. WRV results also indicate that there is a change in the cell wall structure, which affects the capacity of the cell wall to retain water. Similar findings have been reported by Lohi (2007) in the fiber line study of mill with continuous cooking, that WRV and FSP values measured brown stock pulp decreased, especially between blow samples and first brown stock washing pulp samples, while the fines content was maintained at a constant 1% level.

Fiber Wall porosity and Cell Wall Structure

It seems that the density of the pulp sheet is dependent on the final shrinkage of the fiber cell wall rather than the initial swelling of the cell wall. This supposition is based on the relationship between cell wall thickness/diameter and WRV presented in Fig. 4a and 4b. Therefore, it is hypothesized that while the outer dimensions of the cell

wall increase slightly, the capillary pressure of the pores changes, adducting the cell wall shrinkage and thus sheet bulk. This hypothesis was further investigated with DSC and AFM pore size measurements. The pine round-wood pulps were chosen for analysis because they had larger differences in WRV. To research the change in the pore structure of the cell wall, DSC was used to analyze the pore volume of the non-freezing bound water (NFW) and total bound water (TBW = micropore water). The NFW and TBW as a function of pore diameter are presented in Fig. 6.

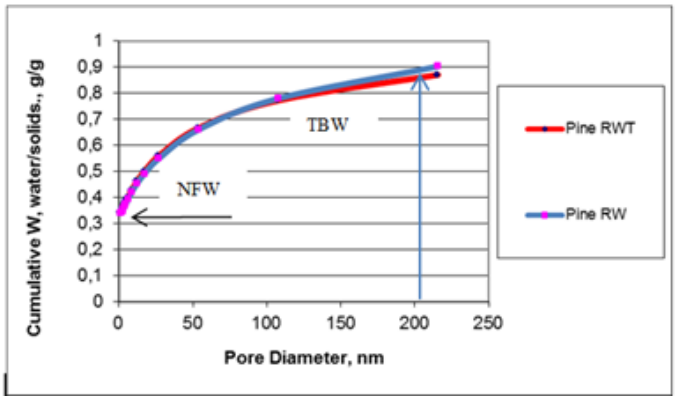

Fig. 6. The pore size distribution volume as a function of pore diameter; the non-freezing (NFW) and total bound water (TBW) are marked in the figure. The results shown are an average of 3 separate DSC runs.

Figure 6 shows a minor difference in the TBW measured with DSC between the treated and untreated pulps. Most notably, there was a slight decrease in the volume at the 200 nm to 216 nm pore diameter area. The measurements were repeated three times, and the amount of non-freezing bound water varied between 0.33 and 0.36 g/g for both pulps. From Fig. 6 it can also be obtained that most of the TBW is in the small pores with diameters of about 100 nm. The reason for the contradiction between WRV and CWT results is probably due to DSC only showing pores of a maximum diameter of approximately 216 nm. WRV is supposed to show the water retained in pores of all diameters.

However, there are measurement and sample preparation issues regarding to the DSC method. According to Borrega and Kärenlampi (2011), the sample pan used for measurement should be equipped with holes for equalizing pressure, which would allow more accurate measurement of the water in macro pores up to 728 nm in diameter. When water in higher pore radius is detectable, it could explain the differences between WRV, DSC, and earlier measured Simmons stain results (Joutsimo 2004). Another aspect which must be taken into consideration is that according to Maloney (1998) the pulp samples are centrifuged at 3000 g to reach the vicinity of FSP of the fibers before DSC measurement. In case of using the DSC method for wood samples, removal of excessive water by centrifuging is not needed; therefore no water is lost from the pores before measurement. In our case the centrifuging might already have removed water from the cell wall pores and therefore leaves pores undetected or they appear to be smaller in the measurement due to removed water. The small deviation in the DSC measurement after 200 nm pore radius between Pine RW and RWT (Fig. 6) could be an indication of this phenomenon.

For further information, the pore area and cellulose aggregated widths were analyzed from AFM images from the S2 layer of the cell wall, as shown in Fig. 7. The aggregate width distributions of both samples Pine RW and Pine RWT showed width distributions between 5 and 42 nm and average width values near 16 nm. These values are in line with widths *e.g.* reported by Hult *et al.* (2001) (14 to 19 nm) in an NMR study on the effect of cooking on cellulose fibril aggregation.

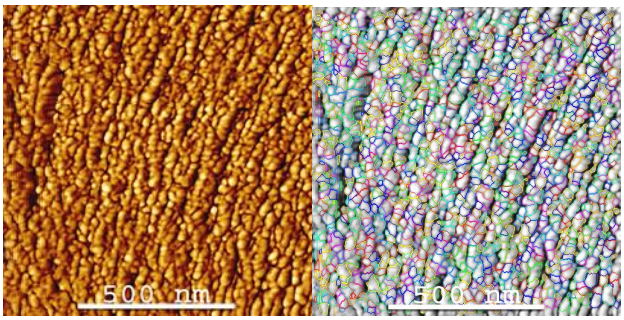

Fig. 7. Left: an AFM phase contrast image; right: the same image after aggregate detection by image processing software. The area of the measurement is 1000 000 nm^2

In Fig. 8 the total pore area of the reference and treated Pine round wood samples are presented.

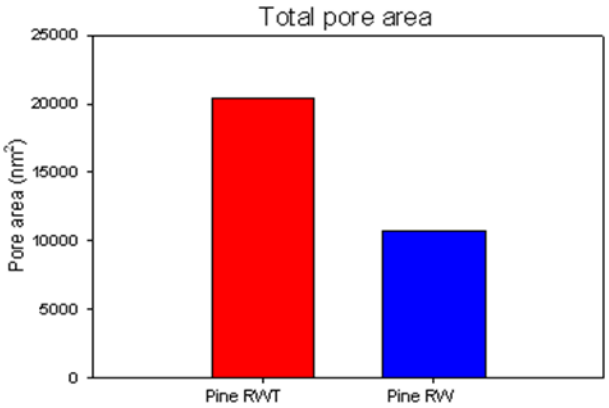

Fig. 8. The cell wall pore area of the unbleached treated Pine and untreated Pine fibers measured with AFM from fiber cell wall cross cuts

Figure 8 shows that the pore area of the cell walls of treated fibers increased, which is in agreement with the hypothesis based on WRV and prior Simmons stain measurements (Joutsimo 2004). From the increased AFM pore area and low WRV values, it can be inferred that when the capillary size increases (and thus the capillary pressure decreases), pores are not able to hold the water inside the cell wall. This decrease in the capillary pressure led to the following effects: a) there was easier water removal at constant g-force in the WRV measurement, b) it probably limited the shrinkage of the cell wall, and c) it decreased the sheet density of the treated fibers.

Results of the fiber diameter and cell wall thickness indicate that they are in line with the detected increase in the AFM pore area. The pore area in the measured area (from Figs. 7 and 8) increased from 1% to 2%. This increase is equivalent to a 1% increase in cell wall cross sectional area, thus 0.5% increase in the cell wall radius.

As a conclusion of the DSC and AFM results, we may argue that in our case, the water content of the pores with a diameter approximately below 200 nm does not affect

the WRV measurement, *i.e.*, in the WRV measurement, the capacity of the cell wall to hold water is defined by pores with a smaller pore diameter than approximately 200 nm.

Kraft Fiber Cell Wall Pore Size and Pulp Sheet Density

Based on WRV, DSC, and AFM results, we may conclude that at least 47% of the cell wall structure has the same capillary pressure. The amount of water in the cell wall having the same capillary pressure is the amount of NFW and TBW (0.88 g/g); this is 47% of total water 1.85 g/g (avg. 0.88 (g/g)/1.85 g/g) x 100% = 47.5%). Also, 47% of the total cell wall structure remained unchanged. This is illustrated in Fig. 9.

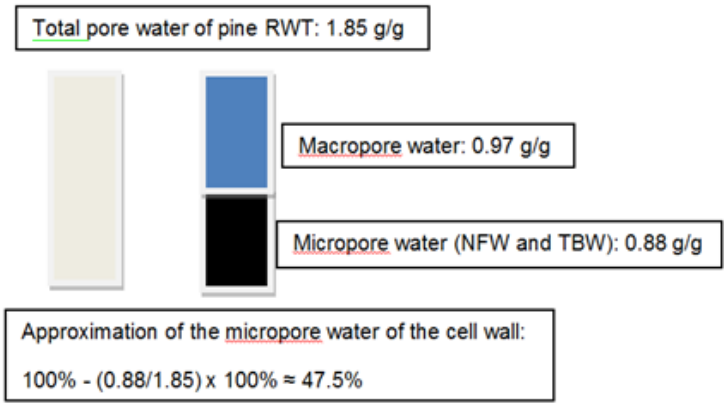

Fig. 9. Pore water of pine RWT pulp in different pore fractions

Despite some measurement issues, it can be assumed that the cell wall does not swell due to capillary pressure. The cell wall remains the same, but the pressure within the cell wall changes depending on the capillary diameter. The capillary diameter will affect shrinkage of the porous structure, the cell wall, and therefore the pulp sheet density.

The capillary shrinkage of porous material has been investigated in material sciences, especially in the area of concrete and glass materials (Dale *et al.* 1998; Hu *et al.* 2007). Surprisingly, capillary shrinkage of the cellulosic materials has not been researched as widely, considering how much the pore structure and pore formation in the cell wall have been studied within pulp and paper industry. Pore shrinkage seems to be an important factor in the formation of the pulp sheet. The main factors affecting pore closure, which can be found in material science literature, are bulk modulus (K) of the porous structure and bulk modulus (K_s) of the solid frame material. Mackenzie (1950) developed a formula for a fully saturated porous medium that has pressure p_{cap} in the pore fluid (Equation 1). The factor of saturation (S', here considered 100% or 1) can also be taken into account. The resulting approximate shrinkage strain equation for partially saturated porous solids is:

$$\varepsilon = \frac{S' p_{cap}}{3}\left(\frac{1}{K} - \frac{1}{K_s}\right) \quad (1)$$

The K and K_s values need to be determined for the fiber. According to Salmen (1982), the bulk modulus of the porous structure (K) is approximately 0.07 GPa. The bulk

modulus of the solid frame material (K_s) can be approximated from the fiber network stress strain curves.

The capillary pressure can be calculated from the equation,

$$p_{cap} = \frac{2 \propto \cos \emptyset}{r} \quad (2)$$

where α is surface tension, which was approximated to be 72.86 mN/m (Pallas and Harrison 1990) between air and water. The contact angle is θ, which was estimated to be 0°. It can be estimated that the part of the fiber walls that have the same micropore volume in the treated and untreated fibers will shrink in the same manner, 47.5% of the cell wall. It can also be estimated that the pore area of the rest of the pores, 52.5% of the cell wall, in the treated fibers in the cell wall has double the area (based on the AFM pore area increase). Therefore the pore radius of the treated cell wall (r_t) in 52.5% of the cell wall is:

$$r_t = \sqrt{2r^2} \quad (3)$$

Table 3 presents the bulk modulus (K) of the porous structure, the bulk modulus (K_s) of the solid frame material, and calculated shrinkage strains (ε, from Equation 1) for material with pore diameters r and r_t.

Table 3. The Bulk Modulus (K) of the Porous Structure and the Bulk Modulus (K_s) of the Solid Frame Material and the Simulated Capillary Pressures

Pulp	***K***	***K*$_s$**
Pine RW	70 MPa	5613 MPa
Pine RWT	70 MPa	2910 MPa
Shrinkage strain ε, with *r* *	-3.43 × 10^{-3} MPa	200 nm (average pore d)
Shrinkage strain ε, with r_t	-2.39 × 10^{-3} MPa	283 nm (average pore d)

*r** = 200 nm

In Table 3, the calculated shrinkage strain ε from Equation 1, in which the capillary pressure has been calculated from Equation 2 is presented. For an r value of 200 nm, the capillary pressure is -3.43 × 10^{-3} Mpa, and for r_t = 283 nm it is -2.39 × 10^{-3} Mpa. The shrinkage strain of pine RWT and pine RW was the same concerning TBW, which was approximately the same for both pulps (Fig. 7). It was 47.5% of the FSP of the pine RWT. The rest of the cell wall of the pine RWT fiber (52.5%) changed structure. Therefore, the shrinkage strain of pine RWT can be calculated as follows,

$$\varepsilon_{Pine\ rwt} = (0.475 \times -3.43 \text{x} 10^{-3}) + (0.525 \times -2.39 \text{x} 10^{-3}) \approx -2.88 \text{x} 10^{-3} \quad (4)$$

in which 47.5% of the pine RWT cell wall shrank without treatment and 52.5% after treatment. Therefore, the relationship between the density of the cell walls of pine RW and pine RWT should be figured in two ways: the proportions of different structures of the cell walls (47.5% and 52.5%) and shrinkage strains of the cell walls. Based on this, 47.5% (Fig. 9) of the pulp sheet density value (apart from the 52.5%) has to have a density value of 662 kg/m^3 (This is the density of untreated sheet pine RW in Fig. 6b), in order to have a final density of 557 kg/m^3 (This density of pine RWT sheet in Fig. 6b).

Also 52.5% of the cell wall has to have lower density, which is equal to the relation of the shrinking strains $\frac{\varepsilon rt}{\varepsilon r}$ (in Table 3) which is 69.7% of the density 662 kg/m^3. This density is 462 kg/m^3. This can be demonstrated by calculating as follows:

$$D_{52.5\%} = \frac{\left(557\frac{kg}{m^3} - 0.475\times 662\frac{kg}{m^3}\right)}{0.525} = \frac{\varepsilon_{\text{pine rwt}}}{\varepsilon_{\text{pine rw}}} \times 662\,\frac{kg}{m^3} \approx 462\,\frac{kg}{m^3} \quad (5)$$

The relationship between shrinkage strains of pine RWT and pine RW should be the same as the relationship between sheet densities of pine RW and pine RWT. This can be demonstrated by calculating simply:

$$\frac{D_{\text{pine rwt}}}{D_{\text{pine rw}}} = \frac{\varepsilon_{\text{pine rwt}}}{\varepsilon_{\text{pine rw}}} = \frac{557\frac{\text{kg}}{\text{m}^3}}{662\frac{\text{kg}}{\text{m}^3}} = \frac{-2.88\text{x}10^{-3}}{-3.43\text{x}10^{-3}} \approx 0.84 \quad (6)$$

Therefore, the pulp sheet density is proportional to the capillary diameter and thus capillary shrinkage of the pulp fiber cell wall. The modulus of the sheet will also be a factor in determining the sheet shrinkage and bulk. Similar predictions have been reported by Allen and Ko (1995), who used log-normal pore distributions and the Laplace equation together with DLVO theory, leading to the conclusion that the distance between lamella, *i.e.* pore diameter, determines collapsibility of the pores. Allen and Ko propose that pores are more easily collapsed with increasing pore diameter. They draw this conclusion based on the observation that pulp dried from water tends to be nonporous and to have lower cumulative pore volume and lower pore width (Stone *et al.* 1968). In order to explain latter, Allen and Ko note that pores with higher diameter should have lower forces of repulsion; this difference would lead to easier collapsibility of the larger pores. An increase in cell wall density by easier collapsibility is somewhat contradictory with the results in that generally, pulp sheet density decreases when repulped, formed into a sheet, and then dried again (Hubbe *et al.* 2007) *i.e.* suggesting less cell wall shrinkage. However, decrease of sheet density could also be attributed to low fiber flexibility due to decreased swelling (Paavilainen 1993; Hubbe *et al.* 2003), and also the change in the fiber shape, curl, kinks and twists could impair consolidation of fibers in the pulp sheet *i.e*. resulting in lower sheet density. On the other hand, the present analysis leads to the prediction that pores with higher diameter have lower shrinkage strain, *i.e*. are less collapsed. Difference between the present predictions and those of Allen and Ko are most probably related to the fiber cell wall pore size measurement. In other words, pores having higher diameter in the pore size distribution might actually increase in diameter during drying. This would decrease shrinkage strain and leave the sheet with lower density. Okayama (2002) has found that repeated drying of fibers and repulping in water leads to increased delamination and cracking of the cell wall. These fibers may have lower WRV and FSP, due to closure of small pores and increase of diameter of larger pores caused by shrinkage strain forces. However, in further research, effects of drying should be studied separately, using the same analytical tools as in this research by, *e.g*., rewetting and drying fiber line simulated fibers with different pore size distributions.

Further research could also focus on the effects of the cell wall structure on the dewatering rates and pulp sheet consolidation. It is also recommended that special care be taken in retaining and monitoring the movement of fines at high vacuum dewatering

while trials are carried out. Also, further research could measure liquid flow resistance or pressure difference over the pulp sheet with fibers having different levels fiber shapes, while applying constant pressure on the sheet. This type of arrangement would potentially avoid fines losses and determine pure effect of fiber cell walls on dewatering resistance and sheet consolidation.

It is clear that further understanding is needed on the effects of fiber cell wall structures, different hemicelluloses contents, and refining of the fibers on capillary pressure-induced shrinkage and its effects on paper product properties.

CONCLUSIONS

1. The calculated shrinkage generated by the capillary forces in different pore cell wall structures was shown to correlate with the sheet density of the fiber network.
2. It was further confirmed that swelling of the cell wall, defined as an increase of the diameter of the cell wall, was not occurring. Rather, the pressure in the cell wall increased, which affected shrinking and flexibility of the fibers.
3. WRV was shown to correlate with the amount of water in the pores with a diameter of at least 200 nm. Changes in the non-freezing and total bound water did not affect the WRV.

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