The Formation of Pores in the Cell Wall

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The purpose of this study was to determine how pores in the fibre cell wall are formed and modified in common pulp fibre processing operations. The pore measurements were done with a novel technique: thermoporosimetry. This technique is based on the fact that water in small pores has a depressed melting temperature. Solute exclusion was also used. Three fractions of water inside the cell wall were found: freezing and nonfreezing water thought to be in relatively small pores (micropores) and bulk water in relatively large pores (macropores). It was found that only micropores are present in wood and mechanical pulp fibres. Macropores are formed by the dissolution of lignin and hemicelluloses in chemical pulping. Beating and hornification affect mostly the volume of macropores, with comparatively little effect on micropores.

La présente étude visait à déterminer comment les pores sont formés et modifiés dans les parois des cellules libériennes lors du traitement ordinaire de la pâte. Les mesures des pores ont été effectuées à l'aide d'une technique novatrice, la thermoporosimétrie. Cette technique est basée sur le fait que l'eau dans les petits pores présente une température de fusion déprimée. L'exclusion par soluté a aussi été utilisée. Trois fractions d'eau ont été trouvées à l'intérieur des parois des cellules : de l'eau congelée et non congelée se trouvant probablement dans les pores relativement petits (micropores) et de l'eau libre dans les pores relativement grands (macropores). Nous avons trouvé que seulement des micropores sont présents dans le bois et les fibres de pâte mécanique. Les macropores sont formés par la dissolution de la lignine et des hémicelluloses lors de la cuisson chimique. Le raffinage et le durcissement a surtout un effet sur le volume des macropores et comparativement peu d'effet sur les micropores.

INTRODUCTION

In recent years the pore structure of the wet cell wall of wood fibres has received a good deal of attention [1–7]. This is appropriate because the "geometry" (size, shape and arrangement) of pores in the cell wall influences many aspects of fibre behaviour. This includes colloidal interactions [4], fibre shrinkage [5] and water removal [6]. Despite the intensity of research activity in this area, the details of fibre pore structure are still not fully known.

Pore measurements are really an attempt to describe the geometry of a solid filled with voids. Relatively basic pore analysis includes the measurement of the pore size distribution and related information, such as the average pore size. Even this measurement is not easy since pores are often irregular in shape and difficult to define by a single number. However, for simplicity the pore size is assumed to be represented by a pore radius which is usually calculated from some other measured parameter. This calculation includes assumptions of pore shape and other factors which may be poor approximations. More advanced descriptions of pore geometry and

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topology, not yet available for pulp fibres, can include factors such as connectivity and number of dead-end pores [8].

Because the cell wall is a hydrogel, i.e. the pores exist only when the fibre is water saturated, and the pores are small enough to encumber microscopic investigations, the pore size distribution for pulp fibres is especially difficult to measure. Attempts to prepare dry fibres with intact pores have not met with great success [9]. For this reason, the best techniques to measure fibre pores are directly applicable to the water-swollen fibres. Three of the most important of these are solute exclusion [10], nuclear resonance spectroscopy (NMR) [11] and polymer adsorption [4]. The pressure-plate technique [12] is also a suitable method to measure the pore size distribution of wet fibres, but this will not be discussed here.

A good deal of what is known about fibre pore structure is based on the solute exclusion test [13]. With this technique the accessibility of pores to noninteracting probe molecules is measured. Soluble mono- and polysaccharides ranging in size from glucose to 2×10^6 Dalton dextran constitute a suitable family of probes. It is assumed in solute exclusion that all pores which are larger than the diameter of the probe are completely accessible. However, because water near the pore walls is not available for diluting the probe molecule (depletion effect), and some pores may have limited accessibility to the outside of the fibre, this assumption may be called into question [4]. Despite its limitations, solute exclusion offers a good way to measure the total amount of water inside the cell wall, otherwise referred to as the fibre saturation point (FSP).

NMR has been used to analyze cell wall pore structure by Li and co-workers since the 1980s [11]. The NMR analysis is based on the fact that water near the pore wall has a perturbed dynamic behaviour. With NMR, the pore diameter, which is calculated from relaxation data, equals the pore's volume-to-surface area ratio. This contrasts with solute exclusion where the pore diameter is related to the size of the pore openings. For this reason the pore size distributions from solute exclusion and NMR have different meanings. One of the important contributions of Li's NMR work was to show that pores are elongated along the fibre axis up to several micrometres in length. While NMR is a potentially powerful form of analysis, the interpretation of the data is not straightforward because the results are susceptible to factors which alter the dynamic or magnetic behaviour of the sample.

Polyethylenimine (PEI) adsorption has recently been used to analyze fibre pore structure [4]. Since the PEI probe adsorbs onto the pore wall, this technique does not suffer from depletion effects which bias solute exclusion results. However, the slow creeping of the PEI molecule into the pores (reptation) may bias the results from this method. The PEI analysis indicates that pores in the cell wall are in the range of 40–50 nm. The PEI adsorption data preclude the existence of pores within the range of 3–40 nm, but larger pores with limited accessibility to the outside of the fibre and pores from 1–3 nm may exist. This is at odds with the solute exclusion results which, after recalculation to account for depletion effects, indicate a rather monodisperse pore size distribution of about 10 nm [4].

A differential scanning calorimetry (DSC) technique called thermoporosimetry can be used to measure the pore size distribution of pulp fibres [14]. Although thermoporosimetry has been used to measure the pore size distribution of porous glasses and other substances [15–17], until recently it has not been applied to pulp fibres. This technique is based on the fact that water contained within pores is at an elevated pressure and therefore has a depressed melting temperature. This effect is described by the Gibbs-Thomson equation. One objection in applying thermoporosimetry to pulp fibres is that other effects, such as osmotic pressure, also cause the melting temperature depression of water in the cell wall. A second objection is that in a thermoporosimetry measurement the sample must be frozen, which may alter the structure of the fibres in an unknown way.

It is the purpose of this study to use thermoporosimetry to measure the pore structure of pulp fibres. The thermoporosimetric analysis is then applied to kraft pulping, mechanical pulping, beating and hornification to enhance the understanding of how pores in the fibre wall are formed and modified in these processes.

METHODS AND MATERIALS

Pore Measurements

The thermoporosimetry measurements were done with a Mettler DSC 30. In the technique used in this study, the energy absorbed when water in frozen pulp fibres is melted at incremental temperatures approaching 0°C is measured. The melting energy is assumed to be directly proportional to the amount of melted water. The pore diameter, D, is calculated from the Gibbs-Thomson equation:

$$D = \frac{-4V\sigma_{ls}}{\overline{H}_m \ln \frac{T_m}{T_0}}$$

where V is the specific molar volume of ice, T_0 is the melting point of water at normal pressure, T_m is the melting temperature, $\overline{H}_m$ is the specific melting enthalpy of water and σ_{ls} is the surface energy at the ice–water interface (12.1 mN/m) [18]. In this form of the Gibbs-Thomson equation it is assumed that the pores are cylindrical.

Pulp moisture content, FSP, nonfreezing water and pore volumes are expressed in mass of water/mass of oven-dried pulp.

TABLE I
THERMOPOROSIMETRY MELTING TEMPERATURES AND CALCULATED PORE DIAMETERS

T °C	*D* nm
−30.0	1.4
−10.0	4.2
−5.0	8.6
−2.5	17
−1.2	36
−0.6	72
−0.3	144
−0.2	216
−0.1	433

The melting temperatures which were used in this study and the calculated pore diameters are shown in Table I. For the cotton sample reported in Fig. 2 (see below), slightly different melting temperatures were used in the range −30–0.2°C. The pore size distribution from thermoporosimetry is nearly independent of moisture content above 1 g/g. All samples were measured at a moisture content from 1–3 g/g. Sample size was 1–3 mg. Two measurements were done per test point and the average reported. Further details of the method used for this study are found elsewhere [14]. The most recent developments in the technique are also available [18].

FSP was measured by solute exclusion [13] using a 2×10^6 Dalton dextran polymer (T2000 from Amersham Pharmacia Biotech AB, Uppsala, Sweden).

Pulps

Pulp samples at progressively lower yields were taken at different times in a 3-stage laboratory kraft cook. Never-dried spruce chips were used in the cook. The cooked chips were disintegrated with the minimum required mixing in a household blender. The <100 mesh fines were then separated with a Dynamic Drainage Jar and discarded. This procedure also served to wash the residual cooking liquor from the pulps. All other fractionating in this study was done using a Bauer-McNett classifier.

Never-dried ECF bleached kraft pulp (BSW) was taken from a Finnish mill. This pulp is a mixture of about 70/30 pine/spruce. Some of the BSW pulp was beaten in a PFI mill to different extents and the >50 mesh fraction was separated and collected. Fines were prepared by beating the BSW in a Valley beater for 2 h and separating and collecting the <200 mesh fraction. The hornified pulp was produced by air-drying the >50 mesh fraction of unbeaten BSW pulp, followed by oven drying at 50°C for 4 h. Some of the hornified pulp was then beaten in a PFI mill to different extents. The >50 mesh fraction was separated and collected for analysis.

First- and second-stage spruce thermomechanical pulp (TMP) was taken from

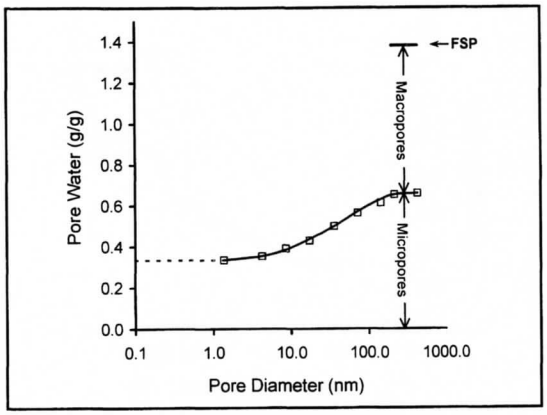

Fig. 1. The cumulative pore size distribution for unbeaten BSW fibres. The "pore water" is the mass of water/mass of solids. The dashed line indicates the quantity of nonfreezing water.

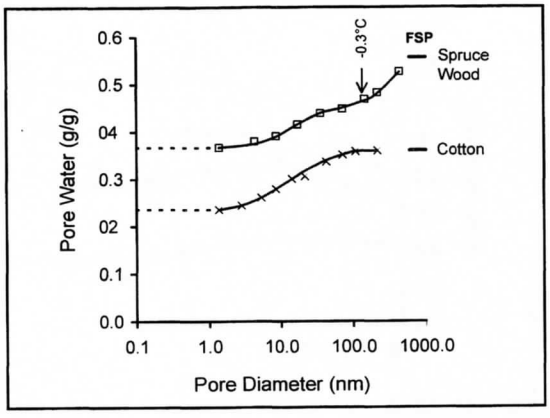

Fig. 2. The pore size distribution for spruce wood (□) and cotton (×). The temperature used to divide macro- and micropores in Figs. 3 and 6 is marked.

just after the refiners in a Finnish mechanical pulp mill. The >0.17 mm shives were removed from the pulp from both stages with a Somerville apparatus and the first-stage shives were saved for measurement. The >50 mesh fraction from both stages was separated and collected for analysis. Groundwood was taken from the accepts stream of the primary screen. This pulp comes from the same mill and was produced from the same raw material as the TMP. This sample was left unfractionated. Both TMP and groundwood were unbleached.

Pulps were washed in 0.1 mol/L HCl followed by deionized water, converted to the sodium form by soaking in 0.1 mol/L sodium acetate overnight, and washed again with twice distilled water. All reported results are for the >50 mesh fibre fraction, unless otherwise indicated.

Wood shavings for FSP measurements were prepared from the chips used in the kraft cook as well as from spruce wood samples taken from the groundwood line.

RESULTS

The Pore Size Distribution for Cellulosic Fibres

The results from thermoporosimetry can be expressed as a cumulative pore size distribution illustrated in Fig. 1 for BSW fibres. The "pore water" on the ordinate of Fig. 1 is the mass of water/mass of solids. The total quantity of water which is detected with thermoporosimetry is represented by the level part of the curve on the right side of the distribution. This is referred to as the total micropore water. Water in the pulp which does not freeze (nonfreezing water) is also detected with this technique. A dashed line on the left side of the distribution indicates the amount of this fraction. Also plotted in Fig. 1 is the FSP. The bar which is used to represent FSP is placed near the end of the distribution so that the amount of water in the cell wall can be easily compared to the total quantity of water detected with thermoporosimetry.

The micropores which are measured with thermoporosimetry are voids within the cell wall where the water has altered thermodynamic properties. This includes both nonfreezing water and water with a depressed melting temperature. It is well known that water in a swollen gel has a depressed melting point. Therefore micropore water includes water which is absorbed into the amorphous regions of the cell wall. It is also a familiar observation that water within sufficiently small pores will also have a depressed melting temperature, as described by the Gibbs-Thomson equation. This implies that micropore water may include water held within small voids inside the cell wall which are outside the amorphous regions.

The amount of nonfreezing water is thought to be related to the number and type of accessible hydration sites [19]. It is appropriate to count nonfreezing water as part of the micropore water because most of the surface area, hence adsorption sites, is probably located here [4].

The difference between the FSP and the micropore water gives the water in the cell wall which has thermodynamic properties similar to bulk water. This water is held outside the amorphous regions of the cell wall in pores which are too large to cause melting temperature depression. It is reasonable to believe that the pores containing bulk water are formed when lignin and hemicelluloses, located between the cellulose microfibrils, dissolve in chemical pulping. The term "macropore" is used to describe these relatively large pores in the belief that they are essentially equivalent to the macropores postulated by Stone and Scallan [9].

If the hypothesis about the formation of macropores is correct then cellulosic fibres which either do not contain lignin, such as cotton, or which have not had the lignin dissolved, such as wood, are not expected to contain macropores. This is confirmed in Fig. 2, where the pore size distribution for cotton reaches a plateau value which corresponds to the FSP. All the water in the fibre wall of cotton is either between the cellulose microfibrils or within the amorphous regions of the microfibrils themselves. Most of the water within the cotton fibre wall is nonfreezing.

For the wood sample in Fig. 2, the pore size distribution does not reach a plateau, but at the highest pore diameter obtainable with this technique the micropore water is quite close to the FSP. To a first approximation all the water within the cell wall of wood fibres is within micropores, although some of the micropores are larger than in cotton. Spruce wood has more nonfreezing water than cotton probably because of the presence of hemicelluloses, which have nonfreezing water in the range 0.5–0.6 g/g [4].

It is useful to define a single point which can be used to estimate the total micropore water. Where the cumulative distribution levels off, for example for BSW pulp, this would ideally be somewhere on the level part of the curve. Because the pore size distribution does not always reach a plateau, and the repeatability gets worse at higher temperatures, the division between micropores and macropores is arbitrarily made at –0.3°C. However, as Fig. 2 illustrates, this slightly underestimates the FSP, and presumably the micropore water, of wood fibres.

Kraft Pulping

An important part of the development of fibre properties in kraft pulping involves the formation of new pores in the cell wall as well as changes to the existing pores. Some idea about the changes to the cell wall pore structure in kraft pulping can be observed in Fig. 3. In the figure the water contained in macro- and micropores is shown as a function of pulp yield.

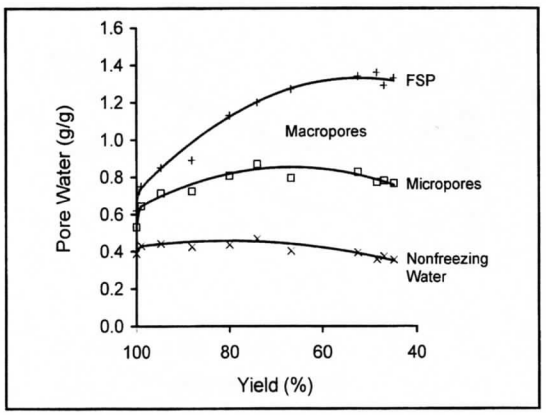

Fig. 3. Pore water for fibres from spruce wood kraft pulped to different yields.

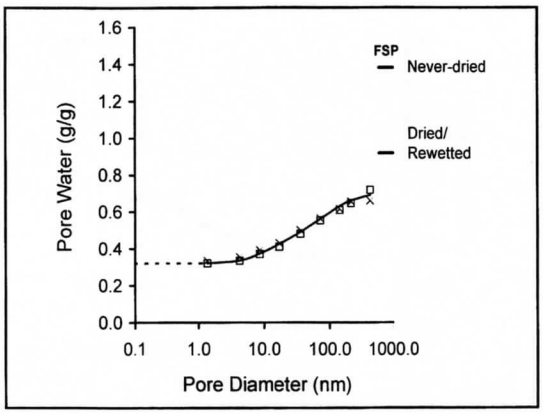

Fig. 4. Pore size distribution for unbeaten, never-dried BSW fibres (×), and the same pulp after a drying cycle (□).

In the unpulped fibres the cellulose microfibrils are believed to be organized into sheets of "interrupted lamellae" with a hemicelluloses/lignin matrix between the lamellae [20,21]. Lignin is a highly cross-linked hydrophobic polymer which restrains the lamellae from separating. The hemicelluloses, on the other hand, tend to promote swelling [22]. When bonds in the lignin are broken, the polymer network, which constitutes the microreticular system, can swell. This happens in the early part of pulping, to about 70% yield. In approximately the same period there is an increase in the nonfreezing water. This may be caused by higher accessibility of existing hydration sites, e.g. by swelling of the cellulose microfibrils. Another possibility is an increase in the number of hydration sites from reactions such as the formation of phenolic hydroxyl groups in the lignin. An increase in hydrophilic sites should facilitate the swelling of the polymer network [19].

After about 70% yield there is a small decrease in nonfreezing water and micropore water. This is probably related to the loss of amorphous material from the cell wall. This may include solubilized lignin, hemicelluloses and amorphous cellulose. The dissolution of amorphous substances from the cell wall increases the fraction of nonswelling, crystalline cellulose. In an earlier study [14], it was found that xylan has about 3× the nonfreezing water and 4–5× the micropore water as microcrystalline cellulose. It is expected that other hemicelluloses are also more swollen and hydrated than wood cellulose. The extent to which degraded and partially soluble lignin contributes to nonfreezing and micropore water is not clear. Earlier it was noted that soluble lignin can have a large effect on both the nonfreezing water and the apparent micropore water [14].

Figure 3 shows that macropores form throughout the whole pulping range, especially below 85% yield. By 45% yield about half the water in the cell wall is in macropores. There is a shallow maximum in fibre swelling at about 50% yield. This is possibly due to the reagglomeration of microfibrils when stresses in the cell wall release [9].

The formation of cell wall pores in kraft pulping has been studied in depth by Stone and Scallan [9]. In the technique which Stone and Scallan used to measure macro- and micropore volumes it was assumed that micropores collapse when pulp fibres are solvent exchange-dried and macropores do not. Ahlgren has used the same technique to measure the pore structure of chlorite delignified spruce fibres [23]. A different method has been used by Ehrnrooth to measure macro- and micropore water [24] for chlorite delignified pulps. In this method it was assumed that drying fibres from the water-swollen state collapses all the macropores and has no irreversible effect on micropores. Ehrnrooth estimated the total pore water and the volume of micropores by centrifuging the pulp pad before and after drying, respectively. None of the above studies offer concrete proof for the existence of macro- and micropores, but rather defines them from the respective measurement technique. Despite this objection, it is interesting to compare the results from these earlier studies to the results from thermoporosimetry.

Stone and Scallan found an average micropore water of 0.59 mL/g which, after an initial rise, was about constant as a function of yield for kraft pulping of spruce [9]. Ahlgren found a nearly constant micropore volume of 0.57 mL/g [23]. Ehrnrooth's measurement of chlorite delignified TMP spruce fibres showed an increase in micropore water from about 0.8–1.0 g/g from 0–66.2% delignification [24]. As Ehrnrooth mentions, the slightly higher volume of micropores in her study, compared to Ahlgren's results, was probably because centrifugation includes some surface water and can therefore overestimate the actual pore water. Another contributing factor may be that the TMP fibres which Ehrnrooth used have a higher micropore volume to begin with than the wood chips which Stone and Scallan and Ahlgren used.

Considering that thermoporosimetry is a completely different technique, the agreement of micropore waters in the present study (see Figs. 1–3) with these earlier studies is good. This indicates that the macro- and micropores measured in each of the studies discussed here have about the same physical basis.

Hornification

When low-yield pulps are dried, there is an irreversible loss of fibre swelling [25–28] which is known as hornification. This is illustrated in Fig. 4 for BSW fibres. It is evident from Fig. 4 that most of the macropores and none of the micropores have irreversibly collapsed when the fibres were dried and rewetted. This suggests that hornification is caused by the formation of bonds, stable to water, between adjacent lamellae. It is likely that both hydrogen and Van der Waals bonds are involved in hornification, however the exact nature of irreversible bonding in pulp fibres has not been established. Since there is no loss in micropore water, it appears that the hydrogen bonding within the microreticular system is largely reversible. Hornification has a negligible effect on the quantity of nonfreezing water. If the formation of an "irreversible" bond involves the displacement of hydration water, then the small change in nonfreezing water may indicate that there are comparatively few direct bonds between collapsed lamellae which prevent the fibre from reswelling.

Beating

It has been shown with both solute exclusion [10] and NMR [11] that one effect of beating is to open pores in the cell wall. The thermoporosimetry results in Fig. 5 also show that pores are opened in beating. In

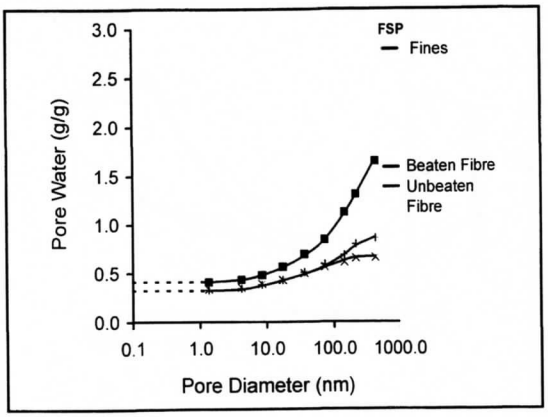

Fig. 5. Pore size distribution for unbeaten, never-dried BSW fibres (×), the same pulp beaten 4000× in a PFI mill (fibres only) (+) and BSW fines (■).

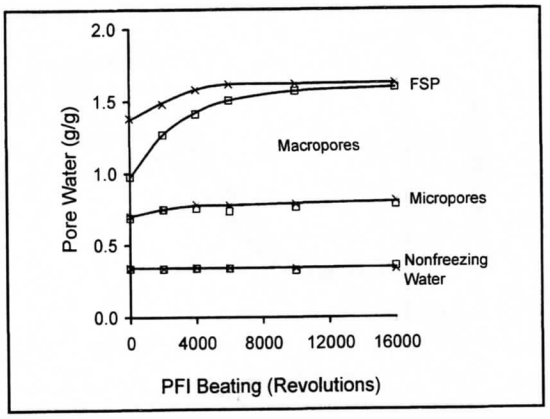

Fig. 6. Pore water as a function of PFI beating for the BSW fibre fraction, never-dried (×) and after a drying cycle (□).

this case the increased swelling of the cell wall is due to an increase in the volume of the larger micropores, above 100 nm. It is unclear from the present data how "larger micropores" relate to the structure of the pulp fibres. However, since the micropore water appears to be related to the gel swelling, it is possible that the increase in micropore volume indicates that beating has disrupted and increased the swelling of the amorphous polysaccharides. The disruption of surface polysaccharides, and subsequent increase in bonding potential, was proposed many years ago as an important part of beating [29–30].

A primary effect of beating is the production of secondary fines. Secondary fines are highly swollen bundles of microfibrils which are torn from the outer fibre surface. In addition to higher macropore water, Fig. 5 shows that fines have much greater micropore water than the parent fibres. Solute exclusion measurements have also shown that that fines have a larger volume of small pores than the parent fibres [10]. Fines have more nonfreezing water than the fibre fraction, which indicates that the fines have a higher number of accessible hydration sites. This could mean that fines have a lower degree of crystallinity than the parent fibres [31]. However, differences in the chemical composition between fines and fibres could also play a role.

In Fig. 6 the nonfreezing and pore water for BSW pulp, with and without a drying cycle, is shown as a function of beating. The micropores in Fig. 6 were determined at –0.3°C, which corresponds to 144 nm in Fig. 5. For the never-dried pulp there is a modest increase in swelling until about 6000 revolutions after which the curve levels off. The small increase in the micropore water follows the same trend. The regeneration of macropores which have collapsed in hornification is an important function of beating a previously dried pulp. This is illustrated in Fig. 6 where the dried pulp reaches nearly the same maximum swelling as the never-dried pulp. One should keep in mind that the effect of beating on the fibre wall pore structure is not completely described by the DSC and solute exclusion measurements. Microscopic evidence indicates that beating opens cracks and delaminations in the cell wall which are larger than the maximum pore size which is measured with the present solute exclusion method [32].

In Fig. 6, nonfreezing water is independent of beating for the never-dried and previously dried pulps. This shows that beating has a negligible impact on the total quantity of hydration water in the pulp. This confirms Campbell's [33] and Stamm's [34] opinions that beating does not increase the hydration of pulp fibres.

We have noted some differences in the way unbleached kraft fibres behave in beating and hornification. These fibres tend to show more extensive opening of micropores in beating than ECF bleached pulp as well as some collapse of the micropores in hornification. The reason for these differences remains unclear. Although these results are not included here, we mention this so that the reader will exercise restraint in extending the conclusions presented here to pulps not included in this study.

Mechanical Pulping

Mechanical pulp fibres can be liberated from wood with a combination of thermal and mechanical energy. Although mechanical pulps have a much lower swelling than never-dried chemical pulps, they do have a somewhat higher swelling than the original wood fibres [35]. The swelling increase that wood fibres undergo in mechanical pulping is of interest because it may be related to fracture and delamination of the cell wall, often referred to as internal fibrillation. Internal fibrillation is an important part in the development of fibre properties which are acceptable for papermaking.

In Fig. 7, the pore size distribution for TMP fibres after first- and second-stage refining is shown. The first-stage shives are assumed to represent the unrefined wood. Figure 7 shows that there is an increase in swelling in the first and second stages and that this is caused entirely by an expansion of the micropores. Pores in the size-range of macropores are not formed by splitting or delamination. Any cell wall delamination has produced pores which are either bigger than the dextran probe, and therefore not included in the measurement of macropores, or small enough to show up as micropores. It appears that larger micropores are made in the second stage than in the first. However, the significance of this is not clear at this time.

The pore size distribution for groundwood whole pulp is shown in Fig. 8. The swelling increase for groundwood is quite large compared to TMP and pores are created throughout the whole size distribution. Recent measurements by Luukko et al. [36] showed that the fibril-rich fines have a high swelling, which is from 1.6–1.7 g/g for purely fibrillar fines. This indicates that the large swelling increase in Fig. 8 is at least partly due to the presence of fines. It is expected that external fibrils on the fibres contribute to the overall swelling since these are basically undetached fines.

Temperatures in mechanical pulping are high enough for lignin to soften and fibre swelling to increase. Therefore it seems possible that the increase in micropore water in Figs. 7 and 8 is related to irreversible swelling. In order to clarify this point, the pore size distribution for spruce wood before and after boiling in water for 15 min was measured. During the boiling, the lignin softens enough that the swelling of the wood is expected to increase about 50% [22]. However, Fig. 8 shows that the swelling increase is completely reversible. This implies that the opening of micropores is related to the mechanical fatigue of the cell

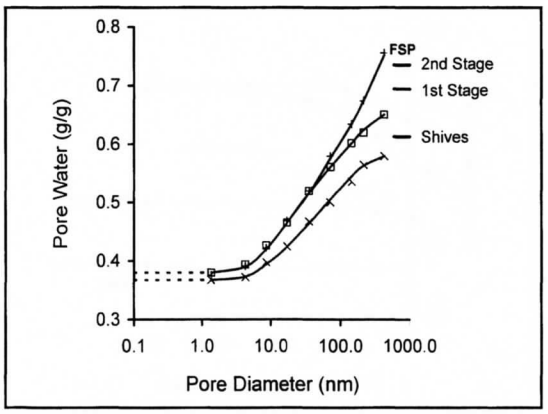

Fig. 7. Pore size distribution for spruce TMP: first-stage fibres (□); second-stage fibres (+); and first-stage shives (×).

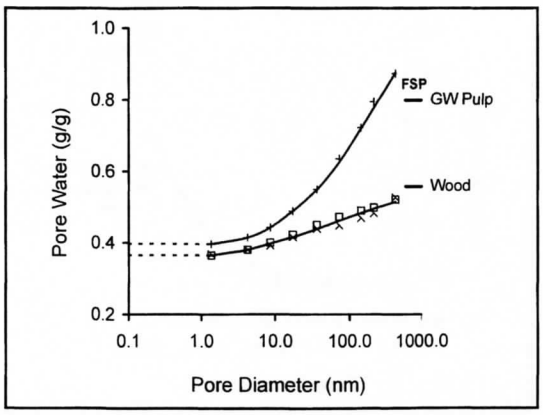

Fig. 8. Pore size distribution for spruce groundwood whole pulp (+) and spruce wood without boiling (×) and after boiling (□).

wall.

Cell wall delamination and damage are readily visible with an ordinary light microscope for mechanical pulps. While these large cracks and dislocations are important for the properties of the finished pulp, they are too large to be measured with the present thermoporosimetry technique. It is possible that the internal fibrillation of the cell wall involves the formation of both large delaminations and much smaller cracks, and it is the small cracks which are detected with thermoporosimetry.

DISCUSSION

Although the results from several different studies suggest that it is reasonable to classify the pores in the cell wall into macro- and micropores, it is not certain if these are really separate nodes on the pore size distribution. For example, in Fig. 1 the cumulative distribution reaches a plateau, implying a bimodal distribution of pores. However, this is not until a pore diameter corresponding to –0.2°C, very close to the melting temperature of the bulk water contained within the macropores. The measurement precision at the end of the distribution is not good enough to be certain if a plateau is reached (the precision depends on the pulp and the melting temperature, for most pulps it is about ±0.1 g/g at –0.1°C and considerably better at lower temperatures).

It is possible that the entire pore size distribution for the cell wall contains other nodes, such as the very small pores, about 2 nm, which Alince and van de Ven have suggested [4]. These pores, which have been identified with gas sorption and the pressure plate technique, occupy a volume of about 0.2 mL/g which implies that they contain only nonfreezing water. Therefore, although these pores cannot be explicitly detected with thermoporosimetry, the DSC data do not preclude their existence. The very large pores, around 1000 nm, which Page has suggested [32], represent a fourth possible class of pores within the cell wall.

A necessary part of the thermoporosimetric measurements is freezing the pulp samples. It is very possible that this may alter the structure of the pulp fibres. Unfortunately, little is known about the crystallisation of water within the cell wall and it is not certain what influence that the freezing has on the measured pore size distribution. While the pore size distribution measured with thermoporosimetry has been shown to be in good agreement with other pore measurement techniques for some systems [15,18], this has not been shown for pulp fibres. It is likely that the relationship between pore size and melting temperature in pulp fibres is more complicated than described by the Gibbs-Thomson equation. The authors' current thermoporosimetry research should help to clear up some of these ambiguities.

CONCLUSIONS

With thermoporosimetry and solute exclusion, the amount of water in macro- and micropores can be measured. Macropores are relatively large gaps in the cell wall where the water has similar thermodynamic properties as bulk water. Water contained in micropores either does not freeze or melts at a depressed temperature. This water is believed to be absorbed into amorphous regions of the cell wall or held within pores small enough to cause melting temperature depression.

In spruce wood fibres all the water is within micropores. In the early part of kraft pulping the FSP, the nonfreezing water, and volume of micropores increases. This is believed to be caused by the breakage of lignin bonds and increase in the number of accessible hydration sites. After about 70% yield the nonfreezing and micropore water decreases. This is probably caused by the dissolution of amorphous material from the cell wall. Macropores are formed throughout the whole pulping range as lignin and hemicelluloses are dissolved from between the cellulose lamellae. The FSP starts from a value of 0.6 g/g in the unpulped wood fibres and reaches a maximum of 1.3–1.4 g/g at about 50% yield.

In hornification (drying and rewetting) of BSW, most of the macropores and none of the micropores collapse. When the hornified fibres are refined, the macropores can be almost completely regenerated.

When never-dried kraft fibres are beaten, there is an increase in fibre swelling and in the volume of larger micropores. Beating does not cause a significant increase in nonfreezing water because beating, under ordinary conditions, does not change the hydration of pulp fibres. Fines have slightly more nonfreezing water than fibres. This may be due to either a lower degree of crystallinity of the cellulose in the fines or to differences in the chemical composition.

It was found that micropores are created in the cell wall in mechanical pulping while macropores are not. It is believed that the opening of micropores is due to the formation of small cracks in the cell wall and that this is related to internal fibrillation. External fibrillation and fines probably also contributes to the increase in pulp swelling in mechanical pulping.

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REFERENCES

1. SUURNÄKI, A., LI, T-Q., BUCHERT, J., TENKANEN, M., VIIKARI, L. and ÖDBERG, L., "Effects of Enzymatic Removal of Xylan and Glucomannan on the Pore Size Distribution of Kraft Fibres", *Holzforschung* 51(1):27–33 (1997).
2. BERTHOLD, J. and SALMEN, L., "Inverse Size Exclusion Chromatography for Determining the Relative Pore Size Distribution of

Wood Pulps", *Holzforschung* 51(4):361–368 (1997).
3. SELENIUS, P. and LINDSTRÖM, M., "Diffusion Controlled Kinetics of Electrolyte Transfer Within the Pulp Fiber Wall: Estimation of the Fiber Wall Pore Structure", The Fundamentals of Papermaking, Transactions 11th Fundamental Res. Symp., 815–836 (1997).
4. ALINCE, B. and VAN DE VEN, T.G.M., "Porosity of Swollen Pulp Fibres Evaluated by Polymer Adsorption", The Fundamentals of Papermaking, Trans. 11th Fundamental Res. Symp., 771–788 (1997).
5. WEISE, U., "Characterization and Mechanisms of Changes in Wood Pulp Fibres by Water Removal", Doctoral Thesis, Helsinki Univ. Technology, Espoo (1997).
6. MALONEY, T.C., JOHANSSON, T. and PAULAPURO, H., "Removal of Water from the Cell Wall During Drying", *Paper Technology* 39(6):39–47 (1998).
7. MALONEY, T.C., LI, T., WEISE, U. and PAULAPURO, H., "Intra- and Interfibre Pore Closure in Wet Pressing", *Appita J.* 50(4):301–306 (1997).
8. DULLIEN, F.A.L., "Porous Media Fluid Transport and Pore Structure", Academic Press, New York (1979).
9. STONE, J.E. and SCALLAN, A.M., "The Effect of Component Removal Upon the Porous Structure of the Cell Wall of Wood. II. Swelling in Water and the Fibre Saturation Point", *Tappi J.* 50(10):496–501 (1967).
10. STONE, J.E., SCALLAN, A.M. and ABRAHAMSON, B., "Influence of Beating on Cell Wall Swelling and Internal Fibrillation", *Svensk Papperstidn.* 19(10):687–694 (1968).
11. LI, T., "Interactions Between Water and Cellulose Fibres. Application of NMR techniques." Doctoral Thesis, Royal Inst. Technology, Stockholm (1991).
12. ROBERTSON, A.A., "Measurement and Significance of the Water Retention Properties of Papermaking Fibers", Consolidation of the Paper Web, Transactions of the Symposium held at Cambridge, 90–118 (1966).
13. STONE, J.E. and SCALLAN, A.M., "A Structural Model for the Cell Wall of Water Swollen Wood Pulp Fibres Based on their Accessibility to Macromolecules", *Cellul. Chem. Technol.* 2(3):343–358 (1968).
14. MALONEY, T.C., STENIUS, P. and PAULAPURO, H., "Hydration and Swelling of Pulp Fibers Measured with Differential Scanning Calorimetry", *Nord. Pulp Paper Res. J.* 13(1):31–36 (1998).
15. ISHIKIRIYAMA, K., TODOKI, M. and MOTOMURA, K., "Pore Size Distribution (PSD) Measurements of Silica Gels by Means of Differential Scanning Calorimetry I. Optimization for Determination of PSD", *J. Colloid Interface Sci.* 171(1):92–102 (1995).
16. HOMSHAW, L.G., "Calorimetric Determination and the Porosity and Pore Size Distribution PSD: Effect of Heat on Porosity, Pore Form, and PSD in Water-Saturated Polyacrylinitrile Fibres", *J. Colloid Interface Sci.* 84(7):127–140 (1981).
17. RENNIE, G.K. and CLIFFORD, J., "Melting of Ice in Porous Solids", *J. Chem. Soc. F1* 73(4):680–689 (1977).
18. MALONEY, T.C., "Thermoporosimetry by Isothermal Step Melting", ISWPC Pre-symposium, Seoul, 245–253 (1999).
19. BERTHOLD, J., "Water Adsorption and Uptake in the Fibre Cell Wall as Affected by Polar Groups and Structure", Doctoral Thesis, Royal Inst. Technology, Stockholm (1996).
20. FAVIS, B.D. and GORING, D.A.I., "A Model for the Leaching of Lignin Macromolecules from Pulp Fibres", *J. Pulp Paper Sci.* 10(5):J139–J143 (1984).
21. KERR, A.J. and GORING, D.A.I., "The Ultrastructural Arrangements of the Wood Cell Wall", *Cellul. Chem. Technol.* 9(6):563–573 (1975).
22. ERIKSSON, I., HAGLIND, I., LIDBRANDT, O. and SALMEN, L., "Fiber Swelling Favoured by Lignin Softening", *Wood Sci. Technol.* 25(2):135–144 (1991).
23. AHLGREN, P.A.V., "Chlorite Delignification of Spruce Wood", Doctoral Thesis, McGill Univ., Montreal (1970).
24. EHRNROOTH, E.M.L., "Softening and Mechanical Behavior of Single Wood Pulp Fibers – The Influence of Matrix Composition and Physical Characteristics", Doctoral Thesis, Univ. Helsinki (1982).
25. KITAYAMA, T., OKAYAMA, T. and OYE, R., "Changes of Chemical Pulp Fibers During Recycling", Intl. Symp. Wood and Pulping Chem., Japan, 3:118–123 (1983).
26. DE RUVO, A. and HTUN, M., "Fundamental and Practical Aspects of Paper-making with Recycled Fibers", The Role of Fundamental Research in Paper-Making, Trans. Symposium held at Cambridge, MEP, London, 195–225 (1981).
27. JAYME, G., "Mikro-Quellungsmessungen an Zellstoffen", *Der Papier-Fabrikant/ Wochenblatt fur Papierfabrikation* (6):187–194 (1944).
28. LAIVINS, G.V. and SCALLAN, A.M., "The Mechanism of Hornification of Wood Pulps", Products of Papermaking, 10th Fundamental Res. Symp., 1235–1260 (1993).
29. GALLAY, W., "Some Aspects of the Theory of the Beating Process", Fundamentals of Papermaking, Trans. Symposium held at Cambridge, 377–387 (1961).
30. GIERTZ, H.W., "The Effect of Beating on Individual Fibres", Fundamentals of Papermaking, Trans. Symposium held at Cambridge, 389–402 (1961).
31. HTUN, M. and DE RUVO, A., "The Implication of Fines Fraction for the Properties of Bleached Kraft Sheet", *Nordic Pulp Paper Res. J.* 81(16):507–510 (1978).
32. PAGE, D.H., "The Beating of Chemical Pulps – the Action and the Effects", Fundamentals of Papermaking, Trans. 9th Fundamental Res. Symp., 1–38 (1989).
33. CAMPBELL, W.B., "A Physical Theory of the Beating Process", *Paper Trade J.* 95: 29–33 (1932).
34. STAMM, A.J., "Bound Water and Hydration", *Tappi J.* 33(9):435–439 (1950).
35. SALMEN, L., TIGERSTRÖM, A. and FELLERS, C., "Fatigue of Wood - Characterization of Mechanical Defibration", *J. Pulp Paper Sci.* 11(3):J68–J72 (1985).
36. LUUKKO, K. and MALONEY, T.C., "The Swelling of Mechanical Pulp Fines", *Cellulose* 6(2):123–135 (1999).

REFERENCE: MALONEY, T.C. and PAULAPURO, H., The Formation of Pores in the Cell Wall. Journal of Pulp and Paper Science, 25(12):430–436 December 1999. Paper offered as a contribution to the Journal of Pulp and Paper Science. Not to be reproduced without permission from the Pulp and Paper Technical Association of Canada. Manuscript received December 29, 1998; revised manuscript approved for publication by the Review Panel June 30, 1999.

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