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THE SWELLING ABILITY OF PULP FIBRES

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ABSTRACT

The swelling of fibres in water has a large impact on the consolidation of the web in papermaking and thus on the properties of the final paper. The water taken up by the fibre is held by many different mechanisms and it is not always clear from the techniques used which quantity of water is being measured. In this report, an attempt is made to obtain more knowledge regarding the water- holding mechanisms of fibres, by studying the amounts of bound water, of pore water and of the total water in the fibres. Effects of delignification, recycling, beating and ion exchange are examined. It is concluded that the amount of bound water is a reflection only of the wood polymer composition of the fibre, whereas the pore water is affected by physical changes of the fibre wall. The ionic charges mainly affect the surface water of the fibre.

INTRODUCTION

The water uptake and swelling of pulp fibres are important factors which have a great influence on the consolidation and bonding of the fibres in the web and are thus important for the final quality of the paper products. This work seeks to deepen the understanding of how water uptake and swelling are affected by different treatments influencing the cell wall structure of wood fibres. In this respect, Inverse Size Exclusion Chromatography (ISEC) [1] is used to analyse the apparent pore size distribution of pulp fibres.

In the case of wood fibre materials, water is held by the fibres in many different ways; in the amorphous polymer parts of the fibre cell wall, in cracks and pores made available to the water molecules by different treatments of the wood fibre, in the lumen and on the surfaces of the fibre, as well as by the fibrillar surface gel. The water held by the wood polymers is bound directly to the different polar groups, the hydroxyls, the carboxyls and, if they are present, sulfonic acid groups [2]. This water is held as non-freezing water or, for some of the water held by the carboxylic or sulfonic acid groups, as "freezing bound" water; water having a freezing point depression. Most of this water is held by the hydroxyl groups which on the average have one water molecule attached to each of them at 92% RH [2]. Apart from this water, the fibres hold free water both in the fibre wall and on the fibre surfaces and water in different kinds of pores in the cell wall, water taken up by entropic effects and due to the osmotic pressure created by the dissociation of ions.

Fibres immersed in water swell until equilibrium is established between the water in the fibres and the water in the surrounding solution, i.e. until the chemical potential of the water is everywhere the same. The degree of swelling depends on the temperature and ionic strength, as well as on the mechanical restraints to swelling of the wood fibre material.

Swelling is a term associated with the volume increase of a material due to liquid uptake or to changes in parameters such as temperature or pressure. Liquid uptake in a material generally results in a change in the specific volume, so that a precise determination of swelling in terms of volume changes requires a measurement of the density of the swollen sample. Generally the swelling is, for simplicity, expressed as the weight gain of the material. [3]

The study of the water uptake of fibres is based mostly on indirect measurements, the exception being the pressure plate method [4] which has nevertheless been used to a rather limited extent. Depending on the technique used, the amount of water held by the fibre will be indicated somewhat differently.

The most commonly used technique, the WRV (Water Retention Value) method, measures how much water is retained by the pulp when it is subjected to a relatively low centrifugal field [5]. The swelling water defined in such a way will however vary depending on the centrifugal field and on the time of centrifugation [3]. When the standard conditions of a centrifugal field of 3000g (g is the acceleration due to gravity) and a centrifugation time of 15 minutes are used, some surface water will still be present although lumen water is removed. Thus the water content determined with WRV will contain all the different types of water that the fibre may hold.

In the solute exclusion method, the water-filled volume of the fibre that is inaccessible to a probe molecule of specified size is quantified [6] by measuring the dilution of a solution of probe molecules when a wet pulp sample is added. It is also possible to determine the water contained in different pores; an apparent pore size distribution, by using probe molecules of different sizes. With the smallest probe molecules used, usually glucose, a considerable amount of water is still determined as inaccessible [7].With the largest polymers used, inaccessible to any pores, the total amount of water held by the fibre is determined. This contains all the types of water, except for lumen and surface water. It has also been demonstrated that the swelling water determined with solute exclusion may equal the water determined by WRV [8].

With Inverse Size Exclusion Chromatography, ISEC [9] [10], it is possible to determine the amount of water contained only in pores of a given size; an apparent pore size distribution is obtained, by eluating a solution of different probe molecules through a column packed with the pulp to be examined. Thus the total pore water determined by ISEC should be less than that determined by solute exclusion or by WRV. It is thus also possible to determine how different treatments of the fibre affects the pore water separately from effect on the total water uptake of the fibre.

Utilising Differential Scanning Calorimetry, DSC, the amount of freezing water in a wet fibre can be quantified. The amount of non-freezing water sorbed by the wood polymers of the fibre may then be determined as the difference between the total water content, given by a weight measure, and the freezing water content [11].

The different kinds of water held by the fibre and the techniques for determining these are schematically listed in Table 1 and illustrated in Figure 1. In this work, different types of water; bound water, pore water and total water have been quantified for some pulps, and the influences on these types of water of various treatments have been clarified. Pulps of different yields were chosen in order to study the effects of delignification, while the effect of drying was investigated by comparing virgin pulps with the same pulps after recycling.

Bound"non-freezing" water	— DSC + weight	Solute exclusion	WRV
Freezing bound water	— DSC + weight		
Pore water	— ISEC		
Free, surface water			

Table 1: Different types of water and methods for characterizing them.

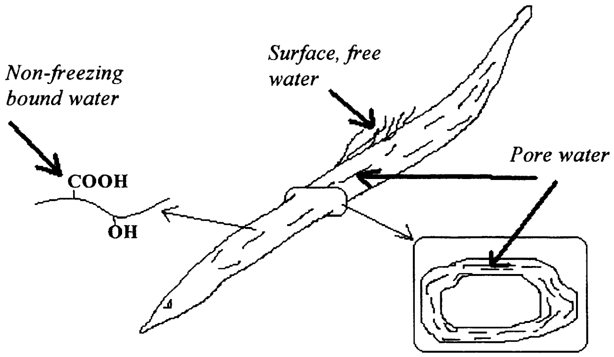

Figure 1: Different types of water held by a wood fibre.

EXPERIMENTAL

Techniques

Inverse size exclusion chromatography, ISEC, was used according to a procedure developed by Berthold and Salmén to determine the amount of water contained in pores of wood fibres [1]. Figure 2 shows a general set-up of the equipment used. A column packed with fibres is eluated with a series of probe molecules, in this case pullulanes, where the relative eluation times are measures of the pore volume.

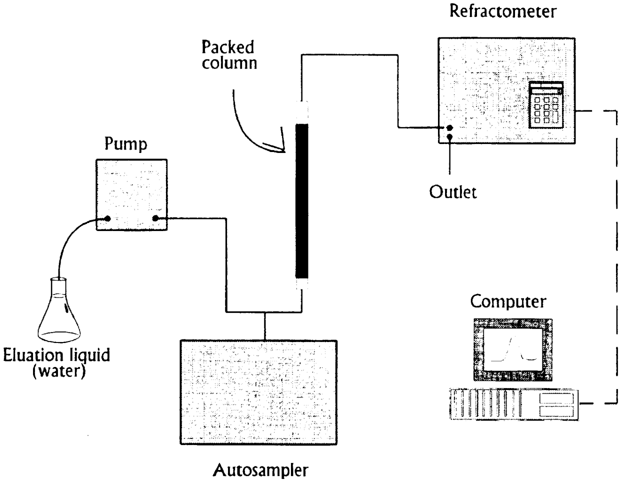

Figure 2: The Figure illustrates in a schematic way the overall set-up of the ISEC-equipment [1].

The column has to be packed with the fibres with great care in order to avoid the development of channels or other deficiencies that will disturb the analysis, see Figure 3. The pulps used were first fractionated according to the Bauer McNett procedure (100 mesh) (SCAN-M6;69) to remove all fines. Typically 3-5 g (dry weight) of the wet pulp were suspended in 12 L of de-ionised water and the suspension was then filtered through the growing column of packed fibres. Vacuum was use to regulate the flow rate to between 50-100 ml/min. The column was finally flushed with de-ionised water containing NaN_3, (0.005 weight%), in order to avoid bacterial growth and to keep the pulp in its sodium form.

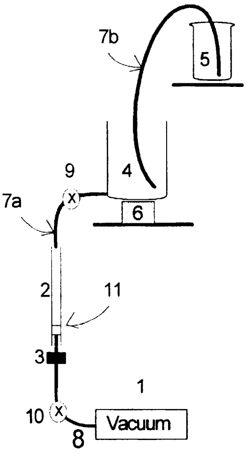

Figure 3: The packing equipment [1].
No. 1 a vacuum pump, No. 2 a Bæckström SEPARO AB 20/270mm column, No. 3, a Bæckström SEPARO AB 20mm column piston design for high flow-rates, No. 4, a 10-12 litre water flask, No. 5, a water container (5 litre), No. 6, a magnetic stirrer, Nos. 7a and 7b polyethylene tubes (inner diam. = 12mm), No. 8, a rubber vacuum tube (inner diam. = 8mm), Nos. 9 and 10 stop valves, No. 11, a 20 x 1 mm polyethylene column filter.

The probe molecules used were pullulanes of different molecular weights (M_w = 5,400 - 1,660,000 and g/mole), stachyose, raffinose, maltose and glucose giving a span of probes with hydrodynamic radii between 4 and 485 Å [1]. The total pore volume (V_{tot}) was calculated according to:

$$V_{tot}=(t_{glucose} - t_0)v/m \qquad (1)$$

where $t_{glucose}$ is the eluation time for the glucose, t_0 is the eluation time for the pullulanes which are too large to enter any pores, v is the pump speed and m is the dry mass of the packed material.

The water retention value, WRV, was determined by centrifugation at 3000g for 15 minutes.

A differential scanning calorimeter, DSC (Perkin Elmer DSC-7), was used, together with a total weight measure, to determine the amount of bound water by recording the amount of excess free water in scans from -70 to 35°C. A scanning rate of 5°C/min. was used with a cooling rate of 200°C/min and a 5 min. equilibrium time at -70°C. Sample weights varied between 15 and 25 mg.

A thermogravimetric analyser, TGA (Perkin Elmer TGA-7) was used to determine the total water content of samples. Approximately 15 -25 mg sample was heated at 5°C/min. from 20 to 130°C.

Materials

Typical market pulps were used in this study;
- a TMP, 100% spruce, peroxide bleached, CSF 59
- a NSSC birch pulp, yield 82%
- a high yield unbleached kraft pulp, kappa 85
- a high yield unbleached kraft pulp, kappa 78.5
- a ECF-bleached (D-EO-D-Ep-D) kraft pulp, kappa 0.5
- a ECF-bleached birch kraft pulp, kappa 12

The wood polymer compositions of the pulps are given in Table 2.

The pulps were supplied in the wet form. Fines, passed 100 mesh, were removed by Bauer McNett. All pulps were ion-exchanged to the sodium form before analysis by stirring in them 2M NaCl. Before the water uptake in the undissociated ionic form was measured, the pulps were stirred in 0.01M HCl to remove all ions bonded to the ionic groups.

Beating was carried out in a PFI mill on pulps in their sodium form.

Recycled pulps were prepared by four times recycling according to the following sequence: sheet-forming, drying at 105°C, repulping, deflaking, washing.

Pulp	Lignin (%)	Hemicelluloses (%)	Cellulose (%)
TMP	27.0	27.1	45.9
recycled	27.1	27.1	45.8
NSSC	21.7	26.0	52.3
recycled	-	-	-
Unbleached, kappa 78	13.5	20.0	67.5
recycled	13.4	18.3	68.3
Bleached, kappa 0.5	0.2	18.6	81.2
recycled	0.4	17.5	82.1
Bleached birch	0.7	25.4	73.9
recycled	0.7	25.1	74.2

Table 2: Wood polymer composition of the pulps.

RESULTS AND DISCUSSIONS

Table 3 gives the different kinds of water determined for three pulps, a TMP, an unbleached kraft pulp and a bleached kraft pulp, thus illustrating the progressive removal of lignin. It is evident that, in the beginning of the lignin removal from the fibre material, the amount of bound water increased, a reflection of an increasing content of amorphous carbohydrates, the hemicelluloses and the amorphous cellulose. In the later state of the delignification when also hemicelluloses have been removed together with the lignin, the remaining wood polymers are less water absorbent; there is a higher content of crystalline cellulose. The pore volume also increased at first, due to the cavities developed when lignin is removed, as was earlier pointed out by Scallan [12]. Extensive removal of the lignin will however, as is evident in the bleached pulp, lead to a collapse of these cavities, lowering the amount of pore water. According to studies using the solute exclusion technique Scallan [12] found a reduction in pore volume below yields of about 55% (kappa ~ 110), i.e. for a yield slightly higher than that of the unbleached kraft here tested. The amount of retained water, as determined by WRV, reflects to some extent the additive effects of the bound water and of the pore water. The changes in the amount of bound water clearly follow that of the pore water, giving a cumulative effect on the WRV.

Pulp	Bound water, DSC (gH_2O/g-dry pulp)	Pore water, ISEC (ml/g-dry pulp)	Retained water, WRV (gH_2O/g-dry pulp)
TMP	0.33	0.80	0.98
Unbleached, kappa 78	0.40	1.31	1.72
Bleached, kappa 0.5	0.33	1.03	1.34

Table 3: Different types of water determined for pulps of different yields.

Figure 4 gives the pore size distribution as determined by ISEC for the three pulps in Table 4. It is evident that, with the progressive removal of lignin, the smaller pores are decreasing while the larger pores are increasing. Thus it is probable that small pores develop into larger ones with the removal of substance. In case of the bleached pulp, it is however also possible that some of the reduction in pore volume in the pore size interval smaller than 22Å is a result of a collapse of the cell wall at low yields.

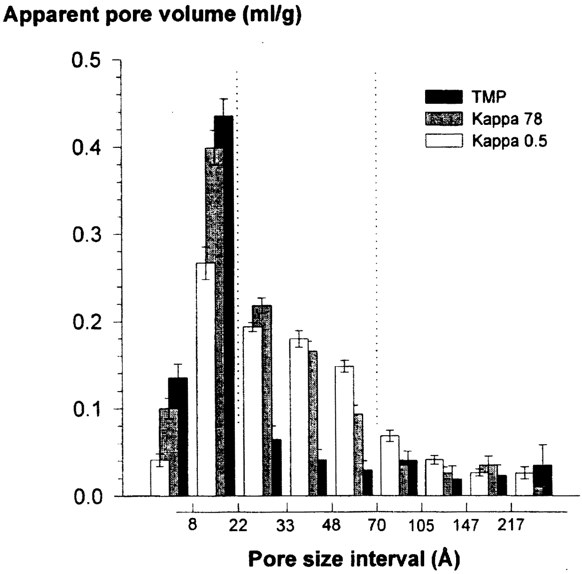

Figure 4: The apparent pore volume in different pore size intervals for three pulps, an unbleached kraft pulp, a bleached kraft pulp and a TMP. The apparent pore size distribution changes as lignin is gradually removed from the pulp. Pore sizes are given in terms of the hydrodynamic radii of the probe molecules. Error bars represent the standard deviation.

The effect of recycling of fibres on the various kinds of water is shown in Table 4. It is evident that the amount of bound water was not at all affected by the recycling. This is a reflection of the relatively unchanged composition of the pulp fibres after recycling compared with that of the nonrecycled ones, see Table 2. The pore volume, as determined by ISEC, had on the other hand for the pulps of low yields been drastically reduced as an effect of the recycling; a closure of pores. In the case of the high yield pulps, the effect on the pores was rather limited. Pores seem to be permanently closed only when some of the lignin has been removed, in agreement with earlier findings based on solute exclusion [13]. Again, the amount of the retained water measured by

Pulp	Bound water, DSC (gH_2O/g-dry pulp)	Pore water, ISEC (ml/g-dry pulp)	Retained water, WRV (gH_2O/g-dry pulp)
TMP	0.33	0.80	0.98
recycled	-	0.73	0.97
NSSC	0.43	1.28	1.45
recycled	0.42	1.27	1.47
Unbleached, kappa 78	0.40	1.31	1.72
recycled	0.42	0.89	1.35
Bleached, kappa 0.5	0.33	1.03	1.34
recycled	0.32	0.68	1.07
Bleached birch	0.30	1.04	1.40
recycled	0.29	0.87	-

Table 4: Different kinds of water for some pulps in their virgin as well as in their recycled states.

WRV was merely the sum of the two other measurements of water, the bound water and the pore water. Thus, in essence, the amount of retained water followed the changes in pore water, the bound water being unaffected, as an effect of the recycling procedure.

The effect of recycling on the pore size distribution is illustrated in Figure *5* for the bleached kraft pulp which shows a typical recycling effect. As a result of the recycling, it was mainly the pores in the pore size interval between 22 and 105Å that were reduced. Small pores were not at all affected by the recycling. The same behaviour was observed by Stone and Scallan [14], although they set the limit of unaffected pores at 12Å (25Å in pore diameter). This swelling water contained in small pores may perhaps be associated with a further water uptake around the bound water sites and thus be contained in pores of a different type than the larger pores. The larger pores created by delignification and beating may be of a more tangential lamellar type whose surfaces

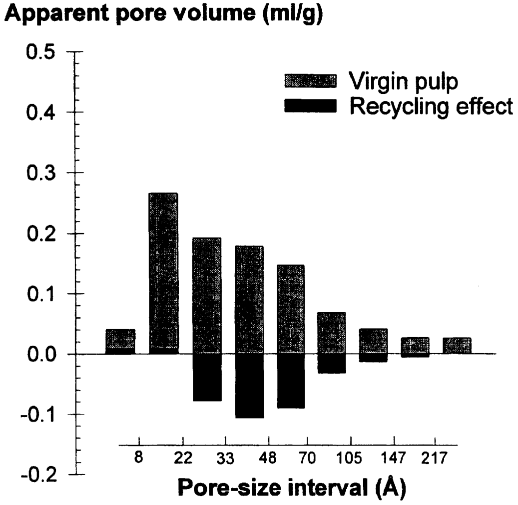

Figure 5: The apparent pore volume in different pore size intervals for the bleached kraft pulp. The darker parts of the bars represent the net effect of recycling on the apparent pore size distribution. The difference in pore volume due to recycling is given for each pore size interval. Pore sizes are given in terms of the hydrodynamic radii of the probe molecules.

may be brought together in a manner which favours the formation of strong intra-fibre bonds inaccessible to water.

In Table 5, the effects of beating and of the ionic form are given for the unbleached kraft pulp, kappa 85. Apparently, the effect of beating on the bound water was very small, as long as the beating was not extensive. The ionic form has a small effect, the dissociated sodium form having a higher amount of bound water than the undissociated proton form. This is a reflection of the carboxylic acids of this pulp which has a charge density of 97 meq/kg irrespective of the beating and agrees well the general behaviour of charged pulps [15]. Beating seemed first to decrease the amount of pore water after which it slightly increased. The initial decrease after which in total pore volume with beating may perhaps be explained by fibre collapse due to the initial loosening of the fibre wall structure by the PFI-beating. Further beating will then reopen these collapsed pores. Only in the case of the unbeaten pulp was there a slightly larger pore volume in the dissociated sodium form than in the undissociated proton form.

Pulp unbleached kraft, kappa 85	Bound water, DSC (gH_2O/g-dry pulp)	Pore water, ISEC (ml/g-dry pulp)	Retained water, WRV (gH_2O/g-dry pulp)
Unbeaten H^+	0.36	1.10	1.50
Na^+	0.38	1.23	1.61
1000 PFI, H^+	0.34	1.02	1.52
Na^+	0.38	1.04	1.67
3000 PFI, H^+	0.40	0.96	1.58
Na^+	0.40	1.01	1.70
6000 PFI, H^+	0.43	1.16	1.64
Na^+	0.51	1.18	1.87

Table 5: Different kinds of water and the effects of beating and ionic form for an unbleached kraft pulp, kappa 85.

The amount of water retained, as determined by WRV, steadily increased with increasing beating in agreement with the general idea that the beating increases the swelling of the fibre [16]. However, in an unbleached pulp, the matrix of the cell wall is still rather intact which means that there are swelling restrictions in the fibre wall so that it will not swell as easily, why beating will have a low effect on the pore volume. For the retained water, there was also a clear difference due to the ionic form, the sodium giving a substantially higher water content than the undissociated proton form. This ionic effect on WRV has earlier been noticed by Lindström and Carlsson [17]. In this case, the amount of retained water did not reflect the sum of the amount of bound water and pore water. This may be accounted for as an effect of the fibrillar surface, which develops with the beating, and where the surface water will also be highly affected by the ionic form of the fibre. In the fibrillar gel of the beaten fibre surfaces, the electrostatic repulsion of the charged groups will have a much greater effect on the water uptake since restricting forces are here small in comparison with those of the interior fibre wall.

Figure 6 shows the effect of the ionic from on the pore size distribution of the unbeaten kraft pulp, kappa 85 when the dissociated sodium form was ion-exchanged to the undissociated proton form. It was mainly the small pores that were reduced. This may be considered reasonable as it is only in the smallest pores that the electrostatic repulsion from charges may be active, increasing the pore dimensions and thus the amount of pore water.

In the bleached pulp, the beating had a much clearer effect on the pore volume, which steadily increased with increasing degree of beating, see Table 6. Beating had no effect on the bound water, as for the unbleached pulp. In comparison with the unbleached pulp, the structure of the cell wall of the bleached pulp is less rigid. A collapse of the structure has already occurred as an effect of the delignification. Beating may thus more easily reopen such pores in the bleached pulp than create new ones, as in the case of the unbleached pulp. It has also been suggested that beating of bleached pulps may remove substances that are trapped in microvoids in the cell wall matrix due to steric hindrance, thus leaving empty spaces detected as pores [18] [19].

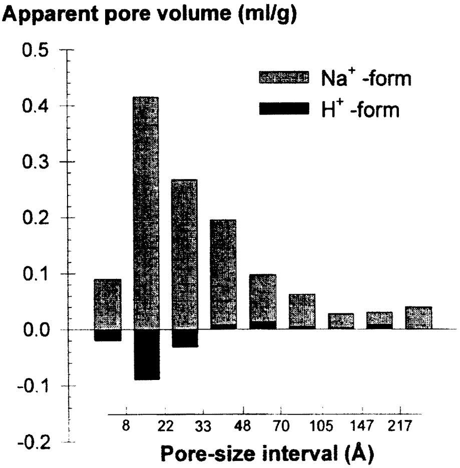

Figure 6: The apparent pore volume in different pore size intervals for the unbeaten kraft pulp in the sodium form. The darker parts of the bars represent the net effect on the apparent pore size distribution of ion exchange to the undissociated proton form. The difference in pore volume due to the ion exchange is given for each pore size interval. Pore sizes are given in terms of the hydrodynamic radii of the probe molecules.

Pulp bleached kraft, kappa 0.5	Bound water, DSC (gH_2O/g-dry pulp)	Pore water, ISEC (ml/g-dry pulp)	Retained water, WRV (gH_2O/g-dry pulp)
virgin	0.33	1.03	1.34
2000 PFI	0.35	1.41	1.54
4000 PFI	0.34	1.64	-

Table 6: Different kinds of water and the effects of beating for a bleached kraft pulp, kappa 0.5.

Figure 7 illustrates the effect of the beating on the pore size distribution of the bleached pulp. Obviously, the pore volume increases over the whole pore size interval, although to a somewhat higher degree for the larger pore sizes.

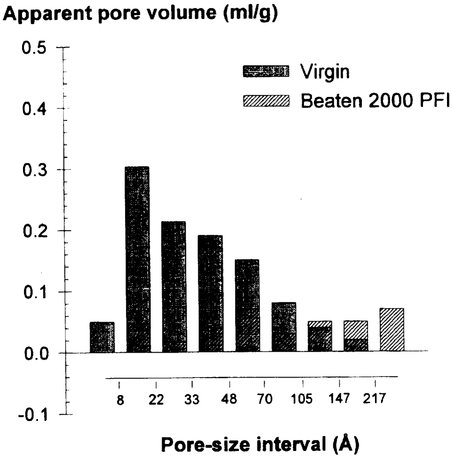

Figure 7: The apparent pore volume in different pore size intervals for the unbeaten bleached kraft pulp. The darker parts of the bars represent the net effect of beating on the apparent pore size distribution. The difference in pore volume due to the beating is given for each pore size interval. Pore sizes are given in terms of the hydrodynamic radii of the probe molecules.

FINAL COMMENTS

It is evident that the water holding capacity of fibres is dependent on the sum of different properties of the fibres. Both the wood polymer composition of the fibre and the physical structure and surface characteristics of the fibre wall have an influence on the water holding capacity.The importance of the different types of water held by the fibre depends on the practical situation considered. Using DSC to determine bound water and ISEC to determine pore water, it is here shown that it is possible to obtain a better knowledge of how different factors influence the water-holding capacity of fibres

Evidently it is only chemical changes in the composition of the fibre and, to some extent, charges that have an influence on the bound water held by the fibre, i.e. held by the wood polymers. On the other hand, physical changes in the fibre wall, giving rise to cracks, have a large influence of the amount of pore water that the fibre may retain. Even if the pore size distribution only is apparent [3], as larger pores contribute to the pore volume measured for the smaller ones, an indication of the changes taking place in the cell wall structure may still be obtained. The ionic charges mainly influence the surface water and thus only affect the total water content determined by methods such as the Water Retention Value, although some effects on the bound water are noticed in a charged pulp.

ACKNOWLEDGEMENTS

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Transcription of Discussion

The Swelling Ability of Pulp Fibres

Dr Lennart Salmén, Head of Fiber Physics, STFI, Sweden

Thad Maloney, Research Scientist, Helsinki University of Technology, Finland

Non-freezing water is a function of the moisture content. Have you kept this (moisture content) constant when you measured it?

Lennart Salmén

The non-freezing or bound water that was presented in the graphs I showed was the amount of water when there is excess water present.

Thad Maloney

What I meant is that I believe that the amount of non-freezing water will also increase if the pulp sample is at a higher moisture content so that you should generally adjust your pulp samples to the same moisture content. I was just wondering if this was done.

Lennart Salmén

The amount of non-freezing water is the only water present when you are in the relative humidity range. This water then steadily increases with relative humidity. This water was determined when we had an excess of about 20% water and we then got reproducible data.

Theo van de Ven, Director, Paprican/McGill, Canada

I have a hard time believing any of your pore size distributions obtained by size exclusion. You show that if you make a geometrical correction that all the pores appear more or less mono disperse and are much larger. If you make another correction, namely that of depletion, which is the fact that non-absorbing molecules don't like to be near surfaces, you again get a completely different distribution. I think you have to be extremely careful in drawing conclusions from size distributions which are in my opinion very unreliable.

Lennart Salmén

I agree that these distributions don't give any absolute values. I emphasised that what is given by ISEC and solute exclusion is only apparent pore size distributions and that it is impossible to correct the results as you don't have a measure of the exact shape of the pores. If we had that we would not have to use these methods at all. Still I think that by comparing the apparent pore size distribution for different treatments you can get some idea of what's happening with the structure of the fibre wall.

Theo van de Ven

I have another question relating to your bound water which according to your measurements is about 0.3cm^2/g of fibre. This is very similar to pore volumes of micropores obtained by solvent exchange. Does this imply that the bound water is sitting in micropores which could be swollen with hemicellulose?

Lennart Salmén

I don't know if one can make that comparison. We have different views here, that of a surface related theory and that of gel swelling. Maybe in the future we can combine these.

Dr Derek Page, IPST, USA

I refer you back to the review of beating and refining I presented at another earlier conference (Cambridge 1989 Symposium). It seems to me that there is lots of water in the fibre wall that you haven't thought about. You've measured the water in pores that are small like 200Å or if you go to solute exclusion up to 500Å diameter. There are pores created in the cell wall when you refine that are enormous. They are 1000Å diameter, even 10,000Å diameter. You can see them in the light microscope. They contain much more water than the bound water and maybe as much as the solute exclusion water. Why did you not mention this water in the very large pores?

Lennart Salmén

In the ISEC method we have used larger molecules to detect the upper limits of pore sizes. As we see it, there is not very much pore volume detected beyond the largest pores that I have reported. The contribution from the largest molecules are zero.

Derek Page

Have you used molecules with a diameter of a micron or so? That's really quite large. Look at the micrographs - they are very easy to see. You can take a beaten fibre and put in on a microscope slide, look at it using polarised light and you will see these gigantic pores.

Lennart Salmén

What troubles me is that if such large pores are present they don't seem to contribute very much to the water retention value.

Derek Page

Well, you may be right. Maybe by the time you have applied large g-forces to the fibre you have squashed that water out. But it's there in the original fibre and you should take account of it.

Lars Ödberg, Vice President Basic Research, STFI, Sweden

This is in response to your question because we have found that in the normal measurement of pore sizes, and we took the sample after water retention value preparation, you definitely don't see big pores. That water has been removed by the water retention value measurement. I think you need a very large pressure to remove that water which is natural.