THE EFFECT OF MECHANICAL TREATMENT ON SOFTWOOD KRAFT PULP FIBERS

Fiber wall

Olli Joutsimo and Leif Robertsén
olli.joutsimo@kcl.fi and leif.robertsen@kcl.fi
KCL, Tekniikantie 2, P.O.Box 70,
FI-02151 Espoo, Finland

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ABSTRACT

In an earlier study the authors found that reduced fiber strength resulting from the mechanical treatment of kraft pulp was caused by changes in the fiber wall, rather than by changes in fiber bonding or fiber deformations.

This study focuses on the nature of the changes in the fiber wall (pore structure) after mechanical treatment. The fiber wall structures of mechanically-treated and untreated fibers were studied in detail using different analytical techniques in order to gain information on the changes in the fiber wall pore structure and fiber wall swelling.

The damage reduced the ability of the fiber wall to hold water, changes that could be measured using water retention determinations and swelling experiments with alkaline iron chloride-sodium tartrate (EWNN, Eisen$^{(III)}$ Weisensäure Natrium-Komplex freier Natronlauge) solution. Fiber wall accessibility was studied by solute exclusion (fiber saturation point, FSP), thermoposimetry and Simons' staining. The strength loss induced by mechanical treatment was concluded to be due to ultra-structural changes in the fiber wall, micropore closure and macropore opening, which also led to changes in water holding ability. A possible reason for the decreased strength of the mechanically-treated fibers could be that there were fewer bonding sites between the parts of the cell wall due to macro pore opening, in contrast to the cell walls of untreated fibers.

TIIVISTELMÄ

MEKAANISEN KÄSITTELYN VAIKUTUS HAVUPUUSELLUKUITUIHIN
Kuituseinä

Aiemmat tutkimuksemme ovat osoittaneet, että havupuusellukuitujen mekaaninen käsittely johti rajuun lujuuden menetykseen, jonka aiheuttivat

pikemminkin muutokset kuituseinässä kuin muutokset kuitujen sitoutumisessa ja deformaatioiden määrässä.

Työssä tutkittiin, minkälaisia muutoksia mekaaninen käsittely aiheuttaa kuituseinän rakenteeseen. Useita erilaisia tutkimusmenetelmiä käytettiin mekaanisesti käsiteltyjen ja käsittelemättömien kuitujen seinämien tutkimiseen, jotta saataisiin tietoa kuituseinän huokosrakenteesta ja kuituseinän turpoamisesta.

Vaurioituneen kuituseinän vedenpidätyskyky aleni, muutokset voitiin havaita käyttämällä vedenpidätyskykymittauksia ja alkaalista rautanatriumtartraatti (EWNN, Eisen$^{(III)}$ Weisensäure Natrium-Komplex freier Natronlauge) liuosta. Kuitujen aksessibiliteettiä tutkittiin mittaamalla liuenneen aineen ekskluusiota (kuitujen kyllästyspiste, FSP), termoporosimetriaa ja Simons-värjäys-menetelmää. Mekaanisen rasituksen aiheuttaman kuidun lujuuden aleneman pääteltiin johtuvan kuidun hienorakenteessa tapahtuvista muutoksista, mikrohuokosten sulkeutumisesta ja makrohuokosten avautumisesta, jotka myöskin johtivat muutoksiin kuidun vedenpidätyskyvyssä. Mahdollinen syy kuidun lujuuden heikkenemiseen on makrohuokosten avautumisen aiheuttama kuituseinämän osien välisten sidosten määrän alenema.

INTRODUCTION

The strength and other properties of softwood kraft pulp fibers are influenced by the porous structure of the fiber wall. The fiber wall structure is made more porous during kraft cooking when the fibers are liberated from wood by dissolving lignin into the cooking liquors. The void volume of a native softwood cell wall is approximately 0.02 cm^3/g. After kraft cooking (yield 47%) the pore volume of a softwood fiber wall will increase to 0.6 cm^3/g, measured by size exclusion or by nitrogen adsorption of solvent-exchanged pulps /1, 2/.

When referring to fiber wall pore size, the measurement technique has to be taken into account. This is because the different techniques which have been used have given different results. It is reported that Nuclear Magnetic Resonance relaxation measurements can be used for determining pore sizes in the range 65-100Å, depending on the pulp and pulp treatment type /3/. Size Exclusion Chromatography (SEC) has been reported to be limited by the availability of the interior of the fiber wall to polymers of different sizes /4/. This means that if the openings in the fiber wall are smaller than the pore size within it, the volume of the fiber wall will be ascribed big as the opening in the external fiber wall layer as pointed out by Lindström /4/. The porous fiber wall structure formed influences the ability of molecules to move in and out of the fiber wall. The amount of lignin removed, therefore, will, among other factors, determine the size of the openings in the fiber wall as discussed by Stone and Scallan /1/. As mentioned earlier, the openings in the fiber wall will determine the movement of molecules into and out of the fiber wall. This has been studied by Alince and van den Ven /5/ who found that the radius of the openings in the fiber walls limiting the adsorption of cationic polyelectrolyes was

around 500Å. This information has been used, for example, by Maloney /4/ in solute exclusion studies, together with thermoporosimetry, to determine fiber saturation point and pore diameter distribution. According to Maloney /6/ the pore size diameter can vary between 3Å and 6000Å /6/. It seems that the pore size distribution varies depending on the method used.

These changes in fiber wall structure will affect the ability of pulped fibers to conform towards each other during drying of the paper and will affect the strength of the paper so formed. Furthermore, it is reported that fiber swelling affects fiber conformability and flexibility, which in turn affect the strength properties of the fiber network /7/. For example, Lindström /4/ has reported a number of correlations between the swelling values prior to sheet forming and the tensile or burst strength of dried pulp sheets. Andreasson /8/ has shown that there is a relationship between the porous structures of pulp fibers with different yields and pulp sheet strength.

In addition to the fiber wall structure, it has been has been shown that the fiber strength and other fiber properties are affected by fiber deformation (curl and kinks) /9, 10, 11, 12/. The relationship between fiber deformations and strength loss in mechanical treatment has been reported by many researchers /13, 14, 15, 16, 17, 18, 19/. Other fiber strength studies have focused, for example, on different acid hydrolysis treatments /20/ and enzymatic degradation /21/ with cellulases. These studies have shown the relationship between cellulose degradation and fiber strength.

In earlier studies /22, 23/ the authors showed that when pulp was mechanically treated at high temperature and pH, the fiber strength decreased by 20%, measured as zero-span tensile index, or by 40%, measured as tear index at a tensile index of 70 N/mg. The Scott bond values measured for the treated pulp were slightly higher than those of the untreated pulp. The strength decrease could not be explained by fiber shortening or by differences in carbohydrate composition. Neither the cellulose degradation nor the local defects (fiber deformations: curl and kinks) could totally explain the strength decrease resulting from mechanical treatment of kraft pulp fibers. The surface layer studies /24/ of the mechanically-treated fibers indicated that there were structural changes in the surface layer of these fibers. The changes in the surface layer of the mechanically-treated fibers were seen as small changes in elasticity, which were thought to enhance the z-directional fiber bonding (Scott Bond). The studies showed also that there were changes in the accessibility to lignin and xylan antibodies but no changes in the degree of crystallinity or in the degree of conversion of cellulose I_α to I_β. The mechanically-treated pulp had a lower water holding ability, which could not be explained by changes in the fiber charge.

This study concentrates on the nature of the changes in the fiber wall pore structure after mechanical treatment. The mechanically-treated and untreated fiber wall structures /23, 24/ were studied using different analytical techniques to obtain information on the changes in the fiber wall pore structure and fiber wall swelling. The contribution of fiber wall structure to fiber strength properties is also discussed.

Experimental

Material

The two pulps used in this study were produced from a chip mixture containing 65% pine (Pinus sylvestris) and 35% spruce (Picea abies). About 50% of the raw material was sawmill chips. Two conventional laboratory kraft cooks of the chips were carried out in a digester, which was equipped with a mixing propeller. Cooking conditions were identical with respect to temperature, chemical charge and time. The only difference was that one pulp (designated MIX) was mixed at 350 rpm for 15 minutes before the end of the cook whereas the other (designated NOMIX) was not. DEDED bleaching was performed on both pulps before PFI beating. The pulping procedure is presented in more detail in reference 23.

Analytical methods

The water retention measurement was carried out on MIX and NOMIX pulps using different g-forces, to provide an indication of the water holding ability of the fiber network and the fiber wall. Measurements were performed according to SCAN-C62, except that the g-forces were varied from 22-400 m/s^2.

The cell wall structure of the pulps was studied by nitrogen adsorption. Analysis of the isotherm, which is obtained when nitrogen gas is adsorbed onto finely divided and porous solids, gives several quantities, which are related to structure. One is the total specific surface area of the material. Another is the total volume of pores that are accessible to a nitrogen molecule (diameter 3.6 Å) and up to 300 Å in radius. In this study the former was measured according to reference /25/ and calculated by the BET- method (Brunauer, Emmer and Teller method). The pulp samples were dried by liquid exchange according to /25/ and by critical point drying (CPD) according to /26/. In the CPD experiments, ethanol and liquid carbon dioxide were used. The measurements were carried out using a Ströhlein AREA meter II apparatus.

The swelling ability of the NOMIX and MIX fibers was investigated using an alkaline sodium-iron-tartrate cellulose solvent (EWNN). The EWNN method is based on the phenomenon that unbleached kraft fibers swell and dissolute in a manner related to the origin and history of the fibers. The measurements and analysis of the results were carried out according to Hortling /27, 28/. Measurements involved following the swelling of the fibers with time by light microscopy at 0.5, 1, 3, 5, 10, 20, 30 and 60 minutes. The degree of fiber swelling was analysed on a scale from 1 to 8 (8 being dissolved). The results were represented as a function of the log of the time. From this plot the dissolution velocity (measured as the slope) and the degree of swelling (swelling affinity) were determined.

The Fiber Saturation Point (FSP) was measured in duplicate for the bleached and unbleached MIX and NOMIX pulps using the solute exclusion technique /29/ with $2x10^6$ Dalton dextran with a hydrodynamic radius of 52 nm. The measurements were carried out according to /3, 6/. The quantity of freezing and non-freezing water was

determined using thermoporosimetry. The thermoporosimetry measurements were performed at Helsinki University of Technology (Finland) using a Mettler 821 differential scanning calorimeter (DSC) according to /3, 6/.

The porosity of the NOMIX and MIX pulps was determined by light microscopy using the two component Simons' stain technique /30/. The method is based on the size and affinity difference of the two colour components. Fibers were treated with a mixed solution of orange (larger fraction, molar mass of > 25 000) and blue (molar mass 998) dyes. Untreated fibers stain blue and fibers with internal delamination, fibrillation, or fiber damage will stain orange. The blue component has a smaller particle size and can therefore penetrate into the smaller capillaries that are unavailable to the larger orange dye particles. The orange dye has a higher binding affinity for the fiber wall than does the blue dye. The higher binding affinity of the orange dye is related to larger polymers, which have more binding sites per molecule than the smaller molecules /31/. The Simons'-stained fibers of NOMIX and MIX pulps were embedded in resin and ground so that cross-sections could be examined under a light microscope.

RESULTS AND DISCUSSION

The fiber walls of untreated (NOMIX) and mechanically-treated fibers (MIX) /23, 24/ were studied using different analytical techniques in an attempt to relate differences in water retention, fiber swelling and pore structure to fiber strength properties.

Water retention and swelling of the fiber wall

In earlier studies /23, 24/ it was found that the unbleached MIX pulp had a much lower water retention value and higher dryness after centrifugation at constant time than the unbleached NOMIX pulp. Water retention, EWNN and BET methods were therefore used to determine whether there were changes in the fiber wall pore structure that could explain the differences in water retention.

The water retention value was determined for MIX and NOMIX fibers as a function of g-force, in order to provide an indication of the nature of the change in the fiber wall pore structure. The results are presented in Table 1.

Table 1. Water retention values of unbleached MIX and NOMIX pulps using different g-forces.

SAMPLE	G-force, (m/s^2)	22	31	50	100	200	400	WRV*
NOMIX, g^{water}/g^{fiber}		10.1	7.4	5.0	3.3	2.6	2.2	1.8
MIX, g^{water}/g^{fiber}		9.45	6.1	4.5	2.7	2.1	1.8	1.4
Difference, %		6.4	17.6	10	18	19	18	22

* according to standard SCAN-C62

The results in Table 1 indicate that the water retention value of the MIX pulp fibers was lower than that of the NOMIX fibers across the range of applied g-forces. The difference in water retention between NOMIX and MIX pulps increased as the g-force was increased. The increasing difference in water retention could be related to an increase in pore volume of the MIX pulp compared to the NOMIX pulp. Another possible explanation could be that the MIX pulps fibers were less swollen (i.e. they had lost their swelling ability) than the NOMIX pulp fibers. According to Lindström /4/ and Scallan /32/ the water retention of fibers describes the swelling of the fiber wall. However Scallan /32/ suggests that WRV measurements should not be used for highly swollen fibers, because it may be assumed that the more swollen the cell wall is, the more it will be compressed under a given applied force. This could also have been the case in our study.

The swelling of the MIX and NOMIX fibers was investigated using the EWNN-swelling measurement. The results are shown in Table 2.

Table 2. The swelling behavior of the MIX and NOMIX pulp fibers in the EWNN swelling measurement.

	UNBLEACHED PULPS		BLEACHED PULPS	
Parameter	NOMIX	MIX	NOMIX	MIX
Dissolution velocity (slope)	1.07	1.01	1.43	1.57
Swelling-affinity (constant)	1.11	1.59	2.06	2.26

The results in Table 2 show that swelling affinity of both the bleached and unbleached MIX pulp fibers was slightly higher than that of the corresponding NOMIX pulp fibers. According to Hortling /27, 28/ the differences in swelling affinity indicate that there are differences in the outer surface layer of the fibers. This is in accordance with earlier results obtained for the MIX and NOMIX pulps /24/. The dissolution velocity of the unbleached and bleached MIX and NOMIX pulps was approximately at the same level, which according to Hortling /27, 28/ describes mainly the changes in the whole fiber wall. The structural changes in the fiber wall did not obviously affect the dissolution velocity of the fiber wall components from the fiber wall.

The fiber wall structure was also studied using nitrogen adsorption (BET). The nitrogen adsorption result gives the surface area of the sample which, according to Stone and Scallan /25/, correlates linearly with pore volume. The surface areas of the unbleached MIX and NOMIX pulp fibers were measured from liquid-exchanged and CPD-dried fibers. The results are presented in Table 3.

Table 3. The BET surface areas of the unbleached MIX and NOMIX pulp fibers were measured from liquid-exchanged and CPD-dried fibers.

PULP	NOMIX	MIX
BET, liquid exchange, m^2/g	203	201
BET, CPD, m^2/g	308	315

It may be concluded from Table 3 that there were no differences in surface area between the samples. This indicates that there should be no differences in pore volume between the samples. Because of the smaller WRV due, for example, to the opened pore structure of the cell wall, it might have been expected that the MIX pulp fibers would have a smaller surface area than the NOMIX pulp fibers. Possible explanations for this unexpected result could be, for example, that pore closure occurred during the liquid exchange or critical point drying, or that the pores were so large that they were outside the range of the nitrogen adsorption volumetric measurement.

The BET results indicated that there were no differences in fiber wall structure. The EWNN indicated there were only small differences in the swelling of MIX and NOMIX fibers, although there were large differences in the WRV of the pulps. This suggests that in this case the swelling of the fiber wall and the water retention or 'water holding ability of the fibers' were not necessarily related to each other. This was suggested earlier by Scallan /32/. Because of this inconsistency in the results, the accessibility of the MIX and NOMIX fibers was studied using the solute exclusion technique, thermoporosimetry (Differential Scanning Calorymetry (DSC)) and Simons' staining.

Fiber wall accessibility

The structural changes in the fiber wall resulting from mechanical treatment were studied using Simons' staining and a Fiber Saturation Point (FSP) method. These methods are based on polymer accessibility or inaccessibility to the fiber wall, and the results might therefore be expected to describe the pore size of the fiber wall.

Simons' stain is a two-color differential stain that is sensitive to variations in the accessibility of the interior structure of fibers. When, according to Yu /31/, pore size is large enough for the orange to penetrate, the fiber adsorbs the orange stain preferentially because of the stronger affinity, and the fibers appear orange. So, when treated with a mixed solution of orange and blue dyes, fibers with internal delamination, fibrillation, or fiber damage stain orange. Table 4 shows how NOMIX and MIX pulps were affected by Simons' stain.

Table 4. The results of Simons' staining (orange, molar mass >25000; blue, molar mass 998) treatment of DEDED-bleached NOMIX and MIX pulps.

SAMPLE	BLUE %	ORANGE %
Nomix, PFI revs. 0	21	79
Nomix, PFI revs. 1000	11	89
Mix, PFI revs. 0	14	86
Mix, PFI revs. 1000	7	93

Table 4 shows that there was a difference between the NOMIX and MIX pulps in terms of the number of fibers that stained orange. The number of orange-stained unbeaten fibers increased from 79% to 86% upon mixing. The quantity of fibers staining orange increased with beating for both the pulps studied, but the MIX pulp stained more orange than the NOMIX fibers at every beating point. This result indicates that the fiber wall of the MIX fibers had become more accessible (opened pore structure) due to the mechanical treatment.

The solute exclusion method with Dalton dextrans of molecular weight 2x106 was used to determine the Fiber Saturation Point (FSP) of the unbleached and bleached MIX and NOMIX pulps. The advantage of the solute exclusion method is that the fibers can be maintained in a water-swollen state during the measurement. This means that the pore closure resulting from the different drying methods can be neglected. This method has been used widely, for example by Stone /25/, Scallan /32/ and Maloney /3, 6/. The principle of this method /25/ is based on the solute molecule being large enough that it can not enter the porous fiber in the dextran-fiber solution. When the fiber swells the concentration of the dextran in the suspension changes because water and not dextran will enter the fiber wall. From the difference in the dextran concentration, the amount of inaccessible water in the solution can be calculated. According to Stone and Scallan /2/, macro pores are defined as a family of large cell wall pores, which do not collapse upon solvent exchange drying. The smaller pores, which are detected by DSC, are referred to by Maloney /3/ as micropores. The micropores hold two fractions of water: non-freezing water (NFW) and freezing bound water (FBW) /3/. The FSP is the sum of NFW, FBW and water in the macropores.

The FSP and DSC results measured for the unbleached and bleached NOMIX and MIX pulps are presented in Table 5.

Table 5. Fiber saturation point value (FSP), freezing bound water (FBW) and non-freezing water (NFW) values for NOMIX and MIX pulps. Results are presented as grams of water per gram of solids. FSP = FBW + NFW + water in macropores (bulk water). Micropore water (total bound water) = FBW + NFW.

SAMPLE	FSP	FBW	NFW	MICROPORE WATER	MACROPORE WATER
NOMIX (unbleached)	1.47	0.60	0.37	0.97	0.50
MIX (unbleached)	1.18	0.53	0.34	0.87	0.31
NOMIX (bleached)	1.3	-	-	-	-
MIX (bleached)	1.17	-	-	-	-

Table 5 shows that the FSP values obtained for both bleached and unbleached MIX pulps were significantly lower than for the NOMIX pulp. If the WRV and the FSP values of the unbleached pulps are compared, it can be seen that the MIX pulp had lower WRV and FSP than the NOMIX pulp. Table 5 also shows that the volume of the macropores was 35% lower and that of the micropores was 10% lower for the MIX pulp than for the NOMIX pulp. This result indicating a smaller pore volume for the MIX pulp than for the NOMIX pulp, contradicts the Simons' staining results. There might however be factors other than smaller pore volume which could influence the FSP values:

- increased accessibility to the dextran (opening of the pore structure)
- decreased accessibility to water
- the dextran is adsorbed onto the fiber surface

The most probable reason for the lower FSP values of the MIX pulp compared to the NOMIX pulp is a change in the accessibility of the fiber wall pore structure to dextran, because the dextran should be inert to fiber walls chemical structures.

The Simons' stained fibers were also embedded into resin to confirm that the stain had reached the fiber wall, as reported by Yu /31/. Figure 1 shows examples of light micrographs of cross-sections of Simons' stained unbleached MIX fibers (left) and NOMIX fibers (right).

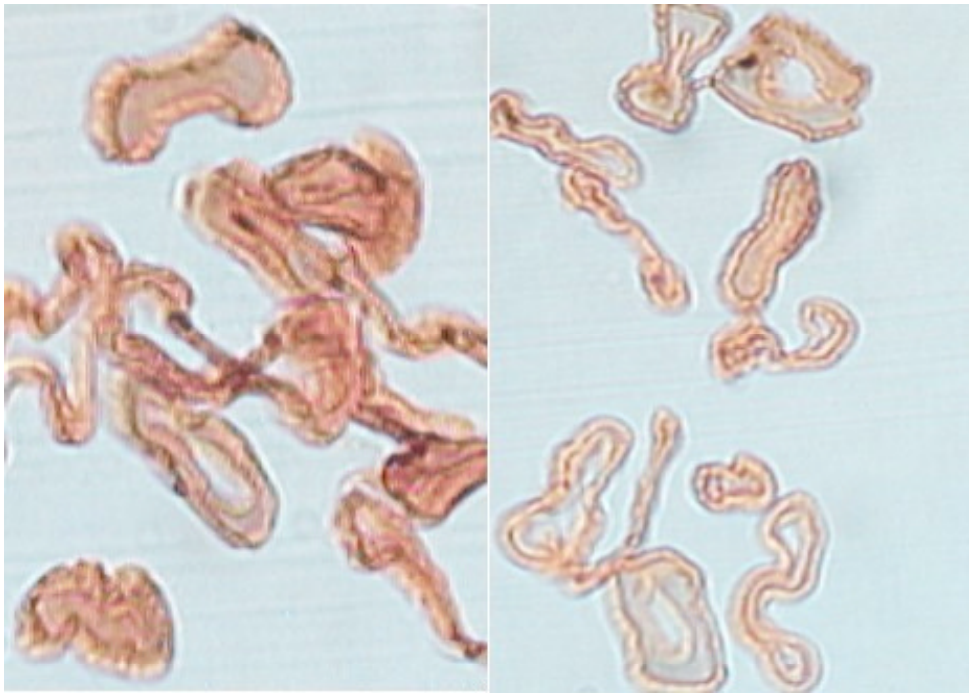

Figure 1. Light micrographs of cross-sections of Simons' stained unbleached MIX fibers (left) and NOMIX (right).

Figure 1 shows that the fibers of the MIX pulp were more intensively and thoroughly stained with the larger orange dye than were the NOMIX fibers. This meant that the fiber wall pore structures of the MIX fibers were more open allowing the large orange dye to penetrate into the fiber wall.

A possible explanation for the lower WRV values of the MIX fibers (Table 1) could be an increase in the amount of accessible water (increased pore size) due to mechanical treatment in mixing. The increased pore size of the MIX pulp fibers could not hold water within the fiber wall under an applied force as efficiently as the pore structure of the NOMIX pulp.

It may be concluded from the results of the WRV, EWNN, Simons' stain and FSP studies that the pore size of the MIX pulp fibers increased as a result of mechanical treatment. The pore structure of the fiber wall had actually opened thereby reducing the water holding ability of the fiber wall.

The results suggested that mechanical treatment during cooking changed the fiber wall pore structure in such a way that the number of links between the porous residues of the fiber wall decreased. The reduced contact between these cellulosic residues of the fiber wall (because of fewer restrictions) affected the cell wall structure so that it could no longer support stresses in the fiber network.

MECHANISM AND CONCLUSIONS

Mechanism

The introduction of mechanical treatment at the end of a laboratory cooking process leads to a dramatic drop in tear strength compared to that of pulp that had not been exposed to mechanical treatment. Tearing work index, damage width, zero span (wet, T70) and fractionation experiments indicated that the mechanical energy did not have a significant effect on the bonding ability, but it did affect single fiber strength /22, 23, 24/.

Subjecting fibers to mechanical energy when they are in a liquid filled state, produces forces or pressure impulses on the fiber wall. Liquid is therefore moved inside the porous fiber wall. Liquid pressure enlarges the capillaries between the macropores, and at the same time causes micropore closure. The enlargement of macropores is seen in the FSP measurements and was also confirmed by Simons' staining.

A schematic drawing of the proposed mechanism resulting in reduced pulp strength is illustrated in Figure 2.

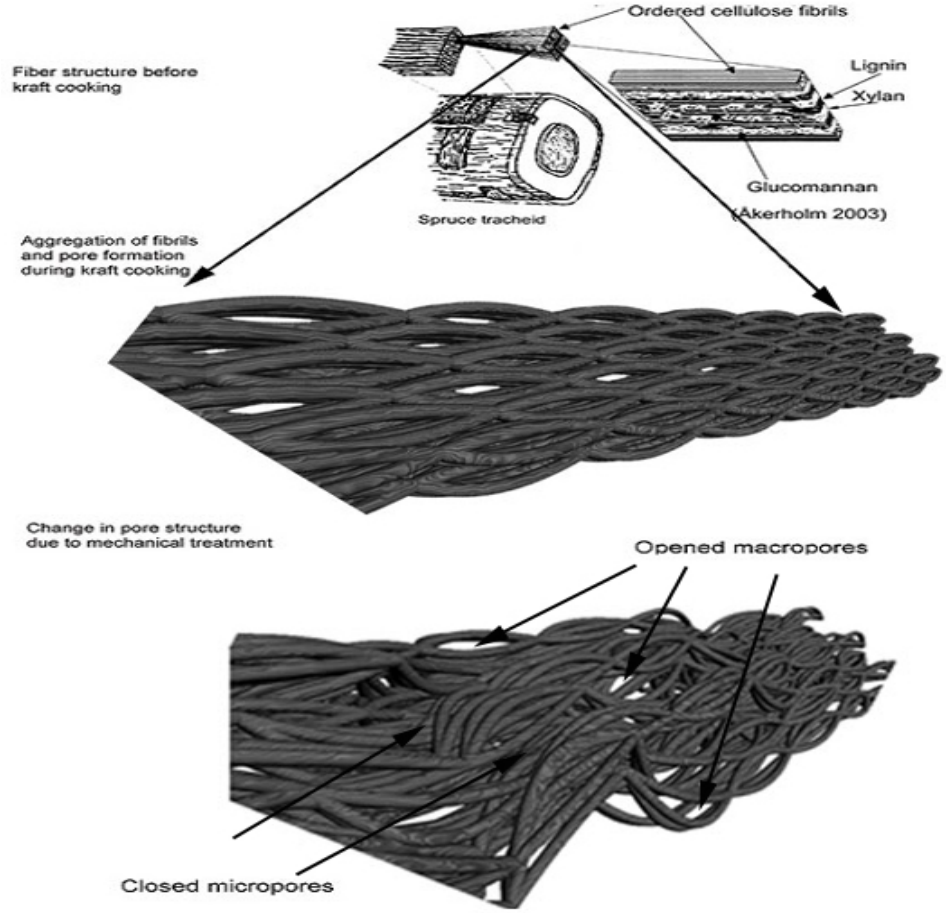

Figure 2. The proposed mechanism of fiber wall destruction.

During kraft cooking the lignin-hemicellulose matrix between ordered cellulose fibrils is dissolved in to the cooking liquor. As the cooking proceeds (i.e. removal of the lignin-hemicelluloses matrix), a void space is created between the fibrils. It has been suggested that the fibrils then aggregate to form larger fibril bundles (aggregates or macro fibrils)/33/. This aggregation of fibrils creates the fiber wall pore structure, i.e. the macropores and micropores. During cooking this pore structure is filled with cooking liquor, dissolved lignin and hemicelluloses. When the porous fiber wall is subjected to mechanical treatment at the end of the cook, the aggregates are further separated from each other. This causes an increase in macropore size but at the same time causes a decrease in micropore size (Figure 2). This capillary enlargement reduces the fiber strength properties, because there will be fewer bonding sites between the aggregates in the cell wall. This decreased internal fiber wall strength would then affect the way in which fibers are able to transfer stresses in the dried fiber network.

Conclusions

The untreated and mechanically-treated fiber walls were studied using different analytical techniques. The main results were:

- The water retention of MIX pulp fibers was significantly lower than that of the NOMIX pulp fibers.
- The EWNN results showed that swelling affinity of both the bleached and unbleached MIX pulp fibers was slightly higher than for the corresponding NOMIX pulp fibers.
- There were no differences in the surface area of the NOMIX and MIX fibers measured using BET for liquid-exchanged and CPD dried fiber.

This study showed that strength loss induced by mechanical treatment was due to ultra-structural changes in the fiber wall, pore (micropore) closure and pore (macropore) opening. The fiber strength decreased because there were fewer bonding sites between parts of the cell wall as a result of mechanical forces compared to untreated fiber cell walls.

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