EFFECT OF MECHANICAL TREATMENT ON SOFTWOOD KRAFT FIBER PROPERTIES

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ABSTRACT

The aim of this work was to gain a better understanding of the changes occurring in softwood strength properties and fiber wall structure after mechanical treatment was applied to the chip/fiber matrix during kraft cooking. Mechanical treatment of fibers during industrial and laboratory production of pulp is common. In the pulp mill the pulp is mixed, pumped and shear forces are applied to the fiber at different temperatures and under different chemical conditions. The main objective of this research was to investigate the reasons for fiber strength loss and to examine the changes that really affect fiber strength.

Fiber damage, changes in the fiber wall structure, reduced single softwood kraft fiber strength and fiber deformations (curl, kinks and dislocations) all affected the fiber network properties.

Mechanical treatment at the end of kraft cooking conditions resulted in fiber damage such that single fiber strength was reduced. This increased with increasing treatment temperature. It was concluded that both mechanical treatment at the end of cooking and homogenisation at room temperature of kraft pulp fibers increased the number of fiber deformations. The increase in fiber deformations did not reduce single fiber strength but did affect the strength properties of the fiber network.

The fiber damage induced by mechanical treatment also decreased the z-directional strength of the fiber network, which was concluded to be due to separation of the structural elements on the fiber surface layer. The separation of structural elements could enhance the irregularities on the fiber surface layer and so reduce the bonding area. The bulking of the fiber surface layer, e.g. more separated layers, might reduce the ability to resist z-directional stresses.

The effect of mechanical treatment on spruce fibers was more severe than on the corresponding pine fibers. The spruce fibers developed more deformations and damage as a result of mechanical treatment. The reasons for the lower bonding and strength properties of the damaged fibers could be due to differences in the fiber wall structures of spruce and pine.

Overall the results suggested that fiber damage induced by mechanical treatment during cooking changed the fiber wall pore structure in such a way that the number of links (between fibrill aggregates) in the fibril (aggregate) skeleton of the fiber wall decreased. The reduced contact in the fibril aggregate skeleton 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.

The zero-span tensile strength of fibers was not dependent on the degree of fiber deformation, but according to the hypothesis presented above, on the 3-dimensional

arrangement of the structural elements in the fiber wall. This 3-dimensional arrangement of the structural elements in the fiber wall defines the axial load bearing ability of the softwood kraft fiber.

CONTENTS

PREFACE

This work was carried out as part of several KCL projects during the years 2001-2004. I am grateful to KCL for allowing me to carry out the work.

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I also thank all my friends for helping me reset my thoughts every now and then.

Finally, I would like to thank my family for their encouragement and love.

Espoo, May 2004

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LIST OF PUBLICATIONS

The thesis consists of this summary and five publications.

I. Joutsimo, O., Robertsén, L. The effect of mechanical treatment on softwood kraft pulp fibers. Pulp and fiber properties. Paperi ja Puu - Paper and Timber 86(2004):5 pp. 359-364.

II. Joutsimo, O., Robertsén, L. The effect of mechanical treatment on softwood kraft pulp fibers. Fiber surface layer. Reviewed and accepted, in 2004, for publication in Pap. Puu.

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V. Joutsimo, O., Wathén, R., Tamminen, T. Effects of fiber deformations on pulp sheet properties and fiber strength. Reviewed and accepted, in 2004, for publication in Pap. Puu.

The roman numerals are used in this summary when publications are referred to.

AUTHORS CONTRIBUTION

The author's role in each of the publications has been the following

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1 INTRODUCTION

The strength properties of cellulosic fibers are very important in the manufacturing of paper and textile-based products. For example, cotton fibers are cellulosic in composition (90-92 %) and are used extensively in the textile, paper and plastic industries. In all these applications the strength, amongst other properties of the cotton fibers, is important. The strength properties have to be met due to requirements set by the production or converting phase or by the requirements set for the use of the end products. The cotton fiber properties and their influence on the production and product properties are well known. This cannot be said of wood fibers. There are still unanswered questions on the relationship between fiber properties and strength properties. In the wood fiber-based industries the strength properties of kraft pulp fibers in particular are important when they are used as reinforcement fibers to improve the runnability of a paper web on a paper machine. This reinforcement pulp is also expected to increase the critical strength properties of the paper. These strength properties are also important in the following converting processes. High strength properties are also of interest because stronger softwood kraft pulps mean smaller demand for pulp wood raw material. If chemical pulp is replaced with mechanical pulp it will result in paper with better optical properties.

In the textile industry the strength of cotton fibers, for example, has been attributed to the fiber structure. This includes the rigidity and high mean of cellulose chain molar mass distribution, the extensive inter – and intramolecular hydrogen bonding, and the highly fibrillar and crystalline structure of the fibers (Hsieh et.al. 2000). Correlations to some extent have been found between tensile strength and the degree of polymerization, spiral angle, fibrillar orientation, fiber birefringence and crystallite sizes (Moharir 2000). Some of the cotton tensile strength properties have also been attributed to the helical ultra structure of the cotton fiber wall. The building blocks of cotton are fine fibrils, which can be slightly separated so enhancing moisture absorption. Each fibril contains about 30 cellulose molecules. Differences in tensile strength come from the various geometrical patterns in which the building blocks are laid down, and from the impregnation with other substances, such as lignins. Cotton cellulose is arranged in a characteristic helical structure in the outer (primary) and inner (secondary) fiber wall layers. The layers of fibrils (in the secondary wall) are laid down at an angle of 21^{o} and the winding of these layers reverses at intervals from clockwise to counterclockwise (from S to Z). The mechanical properties of cotton fibers which make them strong, depend on all the structural features of the fibers (Hearle 2004).

Other natural cellulosic fibers, having high tensile strength, are linen and ramie fibers. However, the relationship between fine structure and tensile properties of these fibers has been studied less than cotton. The moisture absorption of the ramie and linen fibers together with their high molecular weights have been reported to increase the tensile strength and elongation of the samples. The increase in elongation and tensile index are explained by moisture absorption weakening the intermolecular hydrogen bonding force. The weakening of the force enhances the slipping of the amorphous

cellulose chains; fibrils will slip by each other. Consequently, tensile strength increases (Miyake et.al. 2000).

Much work has been done to find correlations between strength properties and viscosity of wood pulps, cotton and cellulose derivatives (Jayme 1942, Musser and Engel 1941). It was found that strength properties of the cellulose derivatives were, as for other polymers, independent of molar mass at high molar masses, but there was a strong influence of the molar mass on the strength properties at low molar masses. Pulp fibers have been reported to behave differently (Rydholm 1965) compared to other cellulose derivatives. This has been explained by the different methods of cellulose degradation (e.g. in cooking and bleaching). The chemical degradation via different kinds of degradation pattern has been reported to give different strength properties at the same average molar mass of cellulose (Gurnagul et.al. 1992, Sjöholm et.al. 2000). The degradation pattern is described to be homogeneous, localized or surface specific degradation. The totally homogeneous degradation has been defined such that the probability of chain scission is the same at all glycosidic bonds and it is not influenced by chain length, crystallinity, fibrillar structure or defects. The degradation is heterogeneous if different glycosidic bonds, within or between cellulose chains, exhibit different reactivities. The heterogeneous degradation of wood can be divided into subtypes with different degradation patterns. Degradation can occur predominantly along weak points throughout the cell wall, for example, by acid hydrolysis (Battista 1956, Gurnagul et.al. 1992, Berggren et.al. 2000) or at the fiber surface, for example, by ozone. According to Molin (2002) and Berggren (2003) the cellulose degradation affects fiber strength only when the cellulose is very degraded to viscosity values below 500 ml/g or Mw (molecular weight) 600 kg/mol for softwoods. Industrially manufactured pulps very seldom have Mw or viscosity values below these limits set by Molin (2002) and Berggren (2003).

The decrease in fiber strength of softwood kraft fibers has been attributed, together with different degradation patterns, to local deformation (also known as damage, defect, distortion) in the fiber wall. These deformations have been reported to arise in the tree as a result of growth stresses. Alternatively, they are generated during processing, for example, in chipping, fiberization or medium consistency unit operations, or in process units in which excess energy is directed to the pulp suspension (Abitz 1991, Bennington et. al. 1989). The deformations have been reported to reduce single fiber strength (Mohlin, et. al. (1990, 1996) and Seth (1999a)).

Along a modern softwood fiber line the preservation of pulp strength has been of great importance because of fiber strength deterioration from discharge through to brown stock handling via oxygen delignification to bleaching (MacLeod 1987 and Tikka 2001). In the industrial processes substantial amounts of energy are expended in mixers and pumps, which result in some reduction in pulp quality. For example, industrial mixers operate with uniform close tolerance between the rotor and stator so that high shear is generated to maximize intense mixing for residence times of the order of hundredths of a second. Tikka (2001) and Clark (1997) have reported that the number of fiber deformations increased along mill fiber lines, but the effect of these deformations on the fiber strength, according to the literature, has been quite inconsistent. Some of these deformations are considered to be beneficial to fiber

strength and pulp sheet strength, but in other circumstances the evidence has not been that clear. To understand the formation of wood fiber strength during cooking and delignification, the formation of the fiber wall structure has to be taken into consideration. The changes in the fiber wall structure due to fiber line unit processes and process conditions and their contribution to fiber strength generation must be better understood.

1.1 Change in the fiber structure during kraft pulping

1.1.1 Softwood fiber structure

Softwood consists mainly (95%) of tracheids (long fibers), the remaining fibrous material being ray cells. A number of models have been presented to describe the detailed structure of the wood fiber (Fengel 1970, Scallan 1974, Fengel and Wegener 1984, Sell and Zimmermann 1993, Brändström 2002). These models suggest that the cell wall consist of different layers, which have different functions in the wood. These cell wall layers P, S_1, S_2 and S_3, have different chemical compositions and thicknesses. The outer layer, primary wall (P) consists of cellulose, hemicelluloses, pectin, protein and lignin. The secondary cell wall is divided into three sub-layers, S_1, S_2 and S_3, all having specific structural arrangements of cellulose. The S_2 –layer of the cell is the largest part of the cell wall, and it is therefore suggested to have the greatest impact on the chemical and physical properties of the fiber. The layered cell wall constitutes a complex biocomposite structure, which is built up of mainly three groups of polymers, cellulose, hemicelluloses and lignin. In addition, softwood fibers contain other polysaccharides, proteins, extractives and some inorganic components. The cell wall matrix of these components is formed so that lignin and hemicelluloses surround the cellulose (Fengel 1971), which is arranged more or less in crystalline regions, called fibrils, microfibrills or elementary fibrils. However, the cellulose fibrils are assumed to be largely crystalline (Rowland and Roberts 1972). It is suggested that these fibrils are arranged in the S_2 layer concentrically (Kerr and Goring 1975) or radially (Sell and Zimmermann 1993). Wickholm (2001) has suggested that cellulose fibrils form aggregates in the native cell wall. The fibrillar structure of the cell wall is built of the cellulose chains. The cellulose chain is a linear polymer of D-glucose residues bound together by β-(1, 4) glycosidic linkages. This structure is responsible for the longitudinal tensile strength of wood fibers. In native cellulose two crystalline forms are found, cellulose Iα and Iβ (Atalla and VanderHart 1984). These Iα and Iβ crystalline cellulose forms differ from one another in that cellulose Iα has a one-chain triclinic unit and cellulose Iβ has a two-chain monoclinic unit cell (Lennholm 1994). Native cellulose also consists of non-crystalline forms, paracrystalline cellulose and cellulose at inaccessible and accessible fibril surfaces (Liitiä 2002). The fibril structure was estimated by Fengel and Wegener (1984) to be 2-4 nm in diameter and formed part of the larger fibril aggregates of 10-30 nm diameter.

The hemicelluloses in this biocomposite material are also polysaccharides, but in contrast to cellulose, they are branched heteropolymers. In softwoods, the principal hemicellulose is galactoglucomannan (about 20%). Its backbone consists of (1→4) linked β-D-glucopyranose and β-D-mannopyranose with α-D-galactose substituents

at C-6. The partially acetylated glucomannan can be divided into two fractions differing in the number of galactose substituents. The ratio of galactose: glucose :mannose is about 0.1:1:4 in the low galactose fraction and 1:1:3 in the high galactose fraction. The former is the dominant component in softwood. Arabinoglucuronoxylan in softwoods (5-10%) has a backbone of (1→4) linked β-D-xylopyranose units (two uronic acid units per 10 xylose units) and at C-3 by α-L-arabinofuranose units (Sjöström 1993).

Softwood lignin consists of the precursor trans-coniferyl alcohol units. These precursors are joined together to form a polymeric macromolecule (Sarkanen and Ludwig 1971). This complex three-dimensional molecule gives a wood fiber rigidity by chemically binding the fibers together, and it enhances resistance towards microorganisms.

1.1.2 Fiber strength and dissolution of wood polymers during kraft cooking

In kraft pulping lignin is degraded by hydroxide ions and hydrogen sulfide ions at high temperatures. Cellulose and hemicelluloses are also partly degraded and dissolved by hydroxide ions under these conditions. The aim in kraft cooking is to dissolve lignin as effectively as possible without cellulose degradation, because cellulose is the load-bearing element of the pulp fiber. According to Gurnagul et.al (1992) and Page (1994) chemical degradation of cellulose results in a fiber with inferior strength properties.

The literature regarding hemicellulose/cellulose content and the relationship to fiber strength is somewhat contradictory. Different experimental conditions have given rise to different relationships between the relative cellulose fraction in the fiber and fiber strength. For example, alkaline extraction of xylan reduced single fiber strength (Leopold and McIntosh 1961.) In other studies the fiber strength/ fiber cross sectional area ratio of kraft pulp fibers was shown to remain constant with decreasing yield (McIntosh 1963). Page et. al. (1985) found a positive correlation between cellulose content and zero-span tensile strength up to a cellulose content of 70-80% (usually bleached kraft pulp contains more than 80% cellulose). Above this level, factors other than cellulose content, such as damaged functionality of the hemicellulose/lignin matrix concerning stress-transfer were thought to be more important. The hemicellulose matrix here functions only to distribute the stresses among the fibrils.

During kraft cooking about 50% of the wood substance is dissolved, the material which goes into solution consisting of lignin and various polysaccharides. The chemistry and topochemistry of this dissolution and its effect on the fiber strength properties have been studied in great detail; however, surprisingly little has been reported on the effect of the changes on the fiber structure and on fiber strength. When the lignin and hemicelluloses are removed during pulping, pores are created in the fiber wall.

The pore volume increases with decreasing kraft cooking yield. Also, the median pore width increases successively with decreasing yield (Stone and Scallan 1968). Stone and Scallan (1967, 1968) called this void space created in pulping between the lamellae (macrofibrils or aggregates) 'macropores' and referred to the intralamellar pores as 'micropores'. Maloney (2000) has studied the formation and modifications of micro- and macropores in kraft pulping of spruce in further detail by measuring pore water after pulping to different yields. Figure 1 shows that the number of different water fractions in the cell wall varies as a function of the pulp yield. The volume of the macropores increases when material is dissolved out of the cell wall. At a yield of 45 % about half the water in the cell wall is in the macropores. Figure 2 shows a pictorial presentation of the formation of macropores in chemical pulping by Goring et. al. (1984).

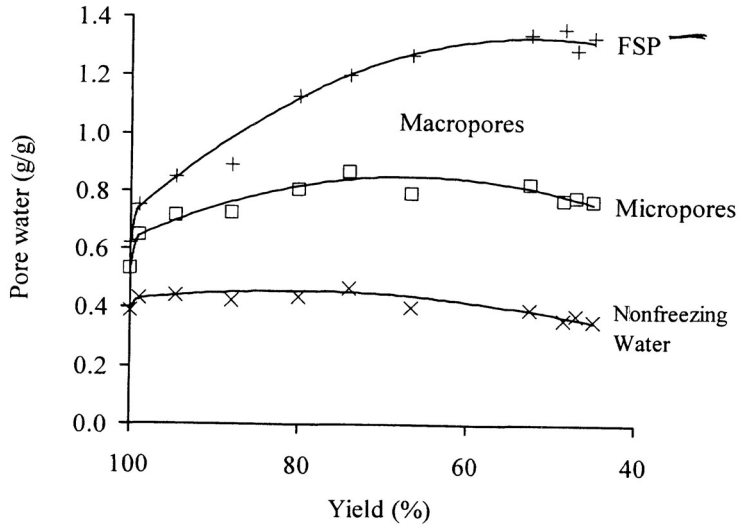

Fig. 1. Changes to the spruce wood cell wall pore structure during kraft pulping (Maloney 2000).

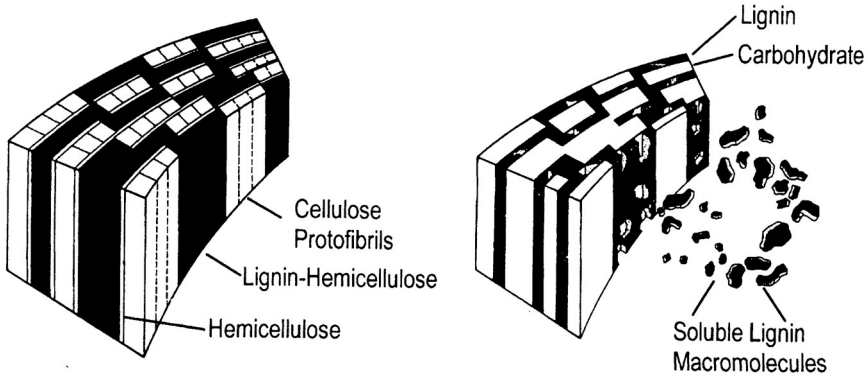

Fig. 2. The dissolution of lignin and hemicelluloses opens up relatively large pores (macropores) between microfibrils (protofibrills) (Goring et. al. 1984).

Duchesne (2000) has proposed that due to the dissolution of the hemicellulose and lignin matrix the fibrillar structures aggregate to larger structural units during pulping. This phenomenon has also been reported by Saka and Thomas 1982, Hult et. al. 2000 and Fahlen 2002. This increase has been measured as average macrofibrillar size (Fahlen 2002). Molin (2002) proposed that this further aggregation has a positive effect on the strength properties of the fibers. Andreasson (2003) has also shown a relationship between porous structures of pulp fibers with different yields and pulp sheet strength.

When trying to understand the pore structure of the fibers and the causes of changes in this structure, it is very important to have a thorough understanding of the charge of the fibers. This has a significant effect on fiber swelling and hence the mechanical properties of the paper prepared from these fibers (Grignon and Scallan 1980, Lindström 1986 and Laine 1996). The charge of softwood fibers is higher with increasing kraft cooking yield (Andreasson 2003). Laine (1996) has reported that increasing fiber charge has a positive effect on the tensile index and Scott bond of pulp sheets prepared from these fibers.

1.2 Fiber strength and pulp production

Fiber strength and fibers lacking damage are highly valued in pulp production. Strength delivery and fiber damage studies have been prompted by the fact that the strength potential of softwood kraft pulps is not usually attained in full mill-scale processes (MacLeod 1987, MacLeod et. al. 1987, MacLeod 1995, Tikka et. al. 2000 and Savolainen 2003). Fiber strength loss in industrial pulp production starts in the wood yard and in the subsequent chipping process, during which damage occurs to the fibers. Fiber strength continues to decrease in the cooking process due to cooking anomalies, and by bleaching when variables (e.g. chemical dosage) are out of control.

The tear and zero-span tensile strength of pulp varies with the amount of juvenile and mature wood. The juvenile wood fibers are shorter and have thinner fiber wall than the mature wood fibers and therefore give pulps with lower tear and zero-span tensile properties. Also, smaller diameter logs tend to have larger percentages of juvenile wood. When the wood is chipped the chip quality is affected by chipper variables such as knife sharpness. Dull knives can crush the end of the chips reducing strength by 5-10%. The cutting speed will also affect chip quality. Possible sites of disorder are microcompressed areas where the knife enters the log. The wood is subjected to extensive axial compressive strain, therefore cracks, dislocations and disorder in both the outer and inner layers of the secondary wall result (Bausch 1960, Hartler 1963).

Variations in chip quality will lead to non-homogeneous chip fractions (e.g. variations in thickness), which will define how they will pulp. Fines, pin chips and thin chips will be overcooked and pulp strength will be lowered. The over-sized chips are too

long and thick for the cooking liquor to completely penetrate. At higher temperatures wood acids in the center of these chips will degrade pulp strength. Undercooked chips will have higher kappa numbers, indicating reduced removal of lignin and lower pulp strength. Thickness is particularly critical. The thicker chip will give lower pulp strength due to the higher kappa and acid attack in the undercooked center. Above a thickness of 5-7mm some strength loss can be expected (Gullichsen et.al. 1995).

Kraft pulp mills operate either batch or continuous digesters or both. Each type has its own system of pre-steaming, packing, impregnation, cooking, washing in the Kamyr digesters and digester discharge. Although the technologies are different, the fundamentals in the pulping of the wood chips are similar. During pulping the effective alkali and hydrosulfide chemicals attack the lignin and remove it. The alkali also attacks the hemicelluloses and to some extent the cellulose. The attack on the cellulose causes a drop in viscosity and strength loss. Pulp strength varies with kappa number and yield (Kocurek 1994).

In addition to chip damage and nonuniformity of kraft cooking, the strength loss has been shown to occur during digester operations. The discharge of batch cooking systems by hot blowing has been reported to reduce fiber strength and therefore various cold blow concepts and more gentle pump discharges have been introduced to preserve fiber strength (Cyr et al. 1989). This made a significant improvement to strength delivery from batch digesters. The introduction of Hi-Heat washing and the cold blow techniques similarly improved the strength delivery for continuous digesters.

The trials carried out using the hanging basket method have indicated that the batch digester discharge reduces pulps strength, because of the depressurizing step in the conventional cooking systems which terminates the mill cook. Pulp strengths for pulps from the basket method have been reported to be as strong as those of pilot-scale pulps produced from the same raw materials. The pulps obtained from the brown stock washer or from a blow line sampler were usually weaker (MacLeod 1987, MacLeod et al. 1987, Tikka et al. 2001, MacLeod 1990, Cyr et al., 1987).

Strength losses of approximately 25% have been reported in the digester house measured as the tear-tensile relationship of typical bleachable-grade softwood. The strength delivery for softwoods from the complete fiber line is reported to be 60-75% from the overall strength (Fig. 3) potential (MacLeod 1995, Tikka et al.2001). Continuous digester tear-tensile strength loss is reported to be approximately 18%, and medium-consistency oxygen delignification was responsible for a 5% loss measured as tear-tensile relationship and 7% loss measured as zero-span. A loss of 5% occurred in the bleach plant.

Tikka et.al. (2001) found that the digester house strength delivery of modern SuperBatch cooking systems could be as high as that of laboratory reference pulp, but the strength deteriorated in the following brown stock operation. Tikka et al. (2001)

hypothesized that it was much easier to lose pulp strength for pulps having initially high strength levels than from pulps that had lost most of their strength potential. Possible reasons for the strength deficit in an industrial pulping environment proposed by Tikka et al. (2001) are, for example, high-efficiency repeated high-shear-forces, machine elements that damage the fiber structure, high concentrations of ions, alkali and high temperatures in the brown stock operation.

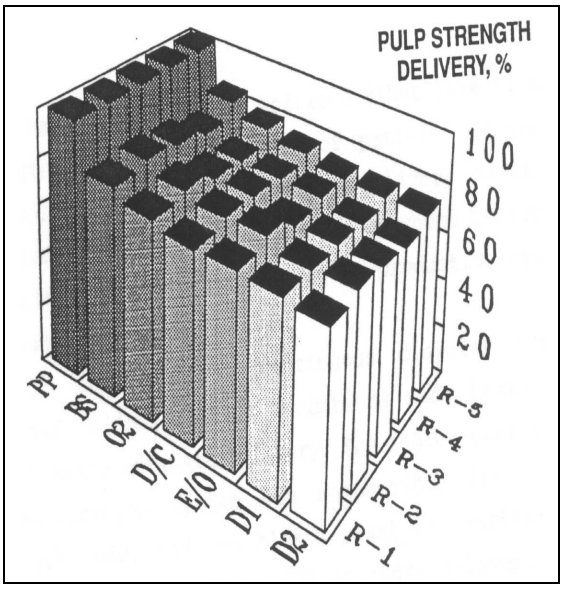

Fig. 3. Typical strength delivery percentages for softwood fiber lines (MacLeod 1995).

Most kraft pulp mills produce bleached kraft pulp utilising medium consistency processes (8-15% consistency). It is known that industrial processing can alter pulp properties by inducing fiber curl and this is especially so where medium consistency and high shear processing is involved (Ellis 1995, Clark et.al. 1997, Bennington et.al. 1989). Medium consistency pulp suspensions behave as non-Newtonial fluids and require substantial energy input for homogeneous processing. The dissipation of this energy in the pulp suspension has the ability to not only induce effective mixing but to modify the pulp fiber physical properties also. De Grace and Page (1976) have reported that increasing extensibility of pulps through the kraft pulp bleach plant directly correlated with the mechanical treatment of fibers from unit operations such as mixing and pumping. According to Ellis et.al. 1997, the physical mixing process appears to be responsible for the reduction in pulp strength as the chemical interactions during mixing had little effect, since the pulp viscosity remained unchanged. Mixing increased the number of fiber wall dislocations and enhanced fiber curl. However, the fiber strength decrease along the fiber line is usually attributed to cellulose degradation and the formation of fiber deformations.

1.3 Fiber deformations and damage

The relationship between fiber deformations and strength loss in industrial cooking systems, and along the fiber line, has been reported by many researchers (MacLeod 1987, MacLeod et. al. 1987, Savolainen 2003, Hägglund 1935, Annergren 1963, Page 1980, Seth 2001, Clark et. al. 1997, Pihlava 1998). Pulp and fiber defects are defined by various types of deformations, for example, fiber curl, kinks and dislocations. Fiber deformations can arise in the tree as a result of growth stresses, or they can be induced in numerous ways during processing, for example in chipping, fiberization or medium consistency unit operations (Abitz 1991, Bennington et. al. 1989). In Fig. 4 the effects of various types of deformations and their effect on the fiber stress-strain curve are depicted. The effects of fiber deformations have been reported to influence the properties of fiber networks (Page et. al. 1980).

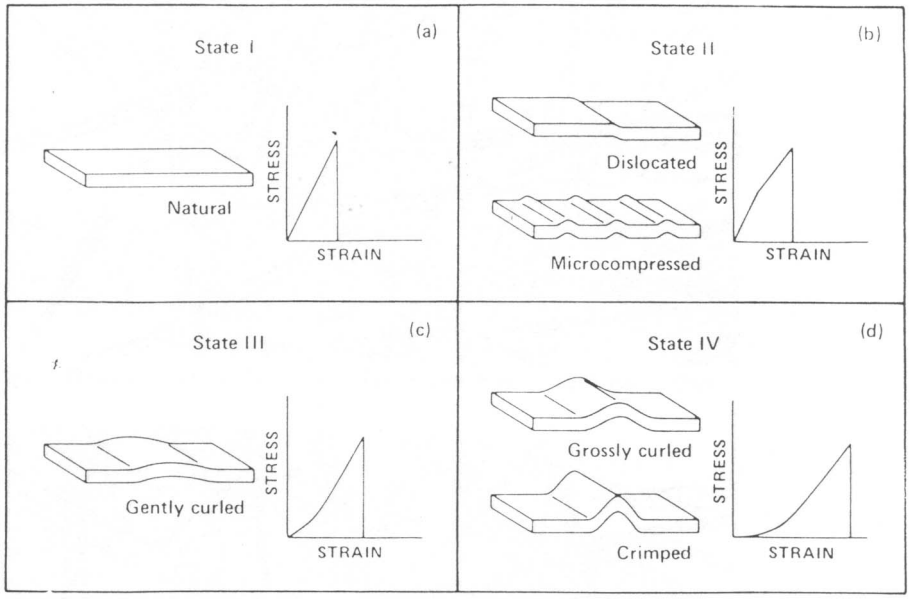

Fig. 4. Various fiber deformation types, described as fibers being in different states, and the corresponding pulp sheet stress-strain curves (Page et. al. 1980).

Fig. 4 shows that pulp sheets made from fibers having dislocated walls strain more than pulp sheets made from intact fibers. According to Kibblewhite (1976) the increase in the number of fiber wall dislocations enhances pulp sheet stretch and tear index. The inducing of fiber kinks and curl increased pulp sheet strain, reduced tensile strength and enhanced tear strength (Page et.al. 1985).

1.3.1 Fiber curl, kinks and dislocations

A numerical value has been assigned to fiber curliness since 1929, when it was introduced as the 'crimp ratio' by Duerden (Page et.al. 1985). The crimp ratio of fibers was measured as the ratio of the end-to-end distance and the fiber contour length. Many different methods for measuring fiber curl have been introduced, for example that of Kilpper, Helle, Kibblewhite and Jordan (Page et.al. 1985). Nowadays the most typical way of describing fiber curl is according to Jordan and Page. In their definition the curl index is a relationship between the fiber contour length and the 'longest dimension', both of which are measured using an image analyser. The longest dimension is the distance between those points within the fiber which are farthest apart (Page et.al. 1985).

Dislocations are according to Hakanen et. al. (1995) and Hartler (1968) a type of deformation described as microcompressions and misaligned zones. Page et. al. (1980) described microcompressions as regions where the alignment of the microfibrils is locally disturbed and, according to Hartler (1963), they develop after the fiber structure has been subjected to a compressive strain above the elastic limit. Local failure will result and a microcompression will develop.

It has been suggested that the disclocated fiber wall changes so that the microfibrils turn within a very small volume with the simultaneous breaking of hydrogen bonds. In such regions it has been proposed that the accessibility of the cellulose is greater in subsequent chemical reactions (Hakanen 1995). Savolainen (2003) suggested that dislocated regions in the fibers enhance polysaccharide degradation by enhanced diffusion of harmful radicals into fiber wall segements, eventually leading to reduced fiber strength. It was speculated that the phenomenon of dislocation was caused by the reduced degree of order in the cellulose or in the internal stresses in the cellulose chains (Hartler 1969). It has also been stated that as a result of dislocations axial shortening of the fiber can be expected (Page et. al. 1985).

A feature of somewhat larger magnitude than the dislocation is the node or crimp. A node is essentially a region of compressive failure with a highly localized compressive strain, often associated with delamination of the cell wall (Page et. al. 1967). Nodes were shown by Forgacs (1961) to be prefentially sited adjacent to ray crossings, presumably because of the tendency for bends to originate there during defibering (Page et. al. 1985). Under some circumstances, fibers will develop kinks at these nodes, so that the direction of the fiber axis changes abruptly at this point (Kibblewhite 1977).

1.3.1.1 Fiber properties and deformations

Pine (*Pinus sylvestris*) and spruce (*Picea abies*) softwood fibers are different in their cell wall structure. Spruce fibers are slightly longer than pine but the cell diameter is approximately the same. The average density of a spruce fiber is slightly lower than that of pine (0.43 g/cm^3 vs. 0.49 g/cm^3) (Fengel et. al. 1984). The average cell wall thickness of latewood fibers is higher for pine than for spruce, but the cell wall thickness of the corresponding early wood fibers is approximately the same for both (Johansson 1940). The slightly lower average density and on average the thicker cell wall of pine fibers indicates structural differences in the fiber cell wall between pine and spruce. Studies have been carried out on the response of pulp fibers to mechanical treatment imparted during medium consistency fluidization as a function of fiber morphology. Results have indicated that medium consistency fluidization induces more curl and microcompressions in thick-walled fibers than in thin-walled fibers. The pulp properties change due to fluidization so that pulp freeness decreases, sheet stretch per unit tensile increases and elastic modulus decreases (Page et. al. 1980, Seth et. al.1995).

1.3.2 The effect of fiber deformations on pulp sheet strength

Fiber curliness mostly affects the tensile strength and the bonding ability of fibers in a fiber network. According to Page et. al. (1985), for example, high fiber curl affects the tensile index so that a sheet formed from such fibers has a low tensile index but can have high tear strength. This has been explained by the uneven distribution of stress along the length of a curled fiber in a fracture zone, curly fibers transferring therefore larger stresses to the bonds which in breaking consume greater energy (Van den Akker 1967). The curly fibers tend to form sheets having a lower elastic modulus and higher stretch than sheets made from straight fibers (Page et. al. 1979).

The low tensile index of curled fibers has also been explained by low fiber segment activation. The concept of activation was suggested by Giertz (1979). According to him, the fiber in the dried sheets can be divided into two zones: compressed, bonded fiber segments, and more or less strained, unbonded fiber segments. The activation is used as a synonym for tightening of the unbonded fiber segments during sheet drying.

Fiber curl, in the absence of other effects, raises the bulk and porosity of the pulp sheet. The curliness of the fibers reduces the drainage resistance of pulps, which is seen as higher CSF values as the fibers become curlier (Page 1985). Curly-fibred pulps are reported to dewater further under a given pressure and vapour is lost more easily on drying (Page et. al. 1985, Hill et. al. 1950).

According to Page et. al. (1979) and Kibblewhite (1977) pulp sheets containing straight fibers have low extensibility both as the wet web and in the dry state. The greater degree of fiber curl also results in more scattering of reflected light, resulting in a matte appearance and slightly higher brightness and opacity (Hill et. al. 1950).

The fiber kinks have been reported to affect the wet strength of the pulp. The more kinked the fibers the higher is the wet rupture energy. It is suggested that chlorine-caustic and chlorine dioxide bleaching cause kinks present in the unbleached fibers to be set into position. Fiber kinking, however, is unaffected by pulp drying stresses Pihlava (1998).

In a dislocated part of the cell wall the alignment of the microfibrils is locally disturbed (Page et. al. 1980). A fiber with no dislocations is extremely stiff. A small number of dislocations suffice to reduce the stiffness significantly. Some delamination occurs in the dislocated regions, which at least partly explains the decrease in the bending stiffness. As a fiber containing dislocations bends it forms a polygon rather than a continuous curve (Hartler 1995, Hartler 1968). Like curl, the presence of dislocations lowers the elastic modulus (Fig. 4) of the sheet (Page et. al. 1979). Dislocations can become weak sites in the fibers, reducing the breaking strength of the individual fibers and the average fiber length (Hartler 1995, Hartler 1968, Mott et. al. 1995). As a result the strength properties of the pulp decrease, as does folding endurance and bursting strength in particular (Hartler 1968). It has also been suggested that the increase in the number of dislocations increases tear strength and stretch. Moreover, dislocations reduce bonding strength by creating discontinuities which are points of bond failure in stressed fiber networks (Kibblewhite1976).

1.3.3 The effect of beating on fiber deformations

Most fiber deformations, curl, kinks and dislocations vanish during pulp beating. This was recognized, for example, by Kibblewhite (1976), Mohlin et. al. (1990), Seth (1999a) , who reported that the strength properties returned to the level of the undeformed pulp. Mohlin et. al. (1996) defined the terms ‘irreversible damage’ and ‘reversible deformation’. Reversible deformation can be removed by PFI beating, where the main effect is the straightening of the fibers. If the zero-span fiber tensile strength is used to measure fiber strength, the measurement should be made on pulps containing only straight fibers. If laboratory pulp is carefully treated so that it consists only of straight fibers, the zero-span tensile index does not change with beating. If the pulp is commercial pulp in which the fibers are deformed, the zero-span tensile index increases initially with beating to reach a plateau after about 3000-4000 PFI revolutions. This increase is due to the fact that the PFI mill straightens the fibers. When the fibers are straight no further change in zero-span is observed Mohlin et. al. (1996).

Mohlin et. al. (1996) also suggested that the irreversible damage could be defined as the difference in zero-span tensile index between an undamaged and a damaged fibre when both are straight, and it could come mainly from chemical degradation during pulping. However, it is possible that it also includes mechanical damage.

The effect of beating on nodes has been discussed by Forgacs (1961), who suggested that soft wood fibers in particular tend to swell, bend and rupture preferentially at the

nodes. The rupture at the nodes plays a significance part in fiber shortening during the beating process. Page et. al. (1967) observed that nodes are severely delaminated in chemical pulps that have not been beaten.

2 OBJECTIVES AND OUTLINE OF THE STUDY

Mechanical treatment of fibers during industrial and laboratory production of pulp is common. At the pulp mill the pulp is mixed, pumped and shear forces are applied to the fiber at different temperatures and under chemical conditions. Very little is known of how mechanical treatment changes the biocomposite structure of a delignified softwood fiber wall. In this study mechanical treatment or input of mechanical energy was carried out by low shear mixing, because it most closely matched industrial applications.

2.1 Objectives and the structure of the study

The main objective of this research was to establish what changes occurred in softwood pulp strength properties and fiber wall structure when mechanical treatment was applied to a chip/fiber matrix during kraft cooking. The aim was to investigate the reasons for the fiber strength decrease and the changes that actually affected fiber strength. The main objective was divided into the following sub-objectives:

1. Determine the effect of mechanical treatment on fiber strength at different temperatures.

2. Determine the effect of mechanical treatment on the fiber surface layer. Study the structural changes within the fiber surface layer and the effects on fiber bonding and fiber strength.

3. Determine the changes in the fiber wall structure of mechanically-treated fibers and examine their influence on fiber strength.

4. Investigate the susceptibility of different softwood fiber wall structures to mechanical treatment.

These sub-objectives are discussed in Chapters 4-5. Chapter 4.1 discusses the effects of the conditions of mechanical treatment on the strength properties of a softwood kraft pulp fiber network and on the fibers (Publications I and V). The mechanically-treated fiber wall layer is discussed in Chapter 4.2 (Publication II). The effects of mechanical treatment on fiber charge and cellulose morphology are discussed in Chapter 4.3 (Publication II). The effects of the fiber wall ultra-structures on fiber strength properties are analyzed in Chapter 4.4 (Publication III). The susceptibility of

different softwood fiber wall structures to mechanical treatment is discussed in Chapter 4.5 (Publication IV). The mechanism of fiber strength deterioration is presented in Chapter 5 (Publication III).

2.2 Outline of the study

This study focuses on the basic mechanism of strength development in softwood fibers and the effect of mechanical treatment on fiber strength. Fiber strength is also influenced by different cellulose degradation patterns and by the average molar mass of the cellulose chain, but these are not discussed in detail in this thesis, because of the minor effect of mechanical treatment on these properties. Wood cell structure, fiber length, fiber surface properties and pulped softwood fiber wall structure are assumed to be associated with fiber and fiber network strength properties.

The experimental methods are described in Chapter 3. Further details are found in Publications I-V. Most of the mechanical tests were carried out according to standard methods, but some non-standard methods were also used.

3 MATERIAL AND METHODS

The details of the experimental set-up and analytical methods used in this study are reported in Publications I-V. The experimental work was carried out using two different types of digester: a forced circulation digester (volume 30 litres) and a laboratory batch digester, which was equipped with a mixing propeller (Fig.5).

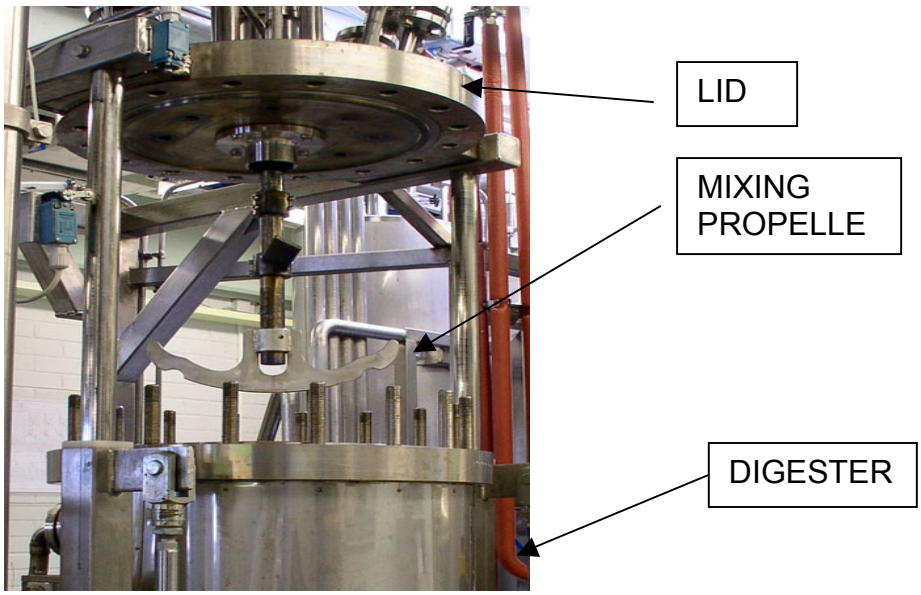

Fig. 5. The laboratory batch digester with mixing device /I/.

The axel beam of the mixing device was fitted through the lid of the digester. The volume of the batch digester was 40 litres. It was heated with hot water, which was pumped through the water jacket surrounding the digester. The temperature inside the batch digester was measured from the end of the mixing plate to ensure that the exact temperature of the contents was obtained. The total amount of energy fed into the cooks during mixing was approximately 20 kWh/t. The tip speed (radius of 0.165m) of the mixing plate was approximately 6 m/s.

3.1 Raw Material

The wood raw material used in the first three phases of this study was industrial softwood (Publications I-III). The chip mixture consisted of 65% pine (*Pinus sylvestris*) and 35% spruce (*Picea abies*). About 50% of the raw material was sawmill chips. The chips thickness was analyzed by screening the chips with slots 0-2mm, 2-4mm, 4-6mm, 6-8mm, 8-10mm and >10mm. The calculated average thickness was 4.8 mm. The chip size was analyzed by screening the chips with holes of diameter 0, 3, 6, 13, 16, 19, 25 and 32mm. The average calculated chip size was 19 mm. The wood raw material used in the first and fourth parts of the study (Publications IV and V) was also spruce (*Picea abies*) and Scots pine (*Pinus sylvestris)* but two types of industrial chips were used: normal round wood chips and sawmill chips. These chip types were chosen to give a wide range of fiber dimensions.

3.2 Mechanical testing

Sheets for testing were made according to ISO 5269-1 from pulps that had not had the fines removed. Kappa number was determined according to SCAN-C 1:77 and viscosity according to SCAN-CM 15:88. Fiber length and fiber coarseness were measured using a Kajaani FS-200. Beating was performed using a PFI beater according to ISO 5264-2 to 500, 1000, 1500 and 2000 revolutions. The apparent bulk density was measured according to EN ISO 5270. Tensile properties were measured according to standard EN ISO 5270, tear index was measured according to standard EN ISO 5270 and zero-span tensile index (from rewetted sheets, Pulmac) was measured according to ISO 15361. Light scattering was measured according to ISO 9416 and Scott bond according to TAPPI T833 (modif.). The water retention value (WRV) was measured according to SCAN-C62.

3.2.1 Symbols

The following abbreviations are used in the text:

- REF: no mechanical treatment.
- NOMIX: stirred during cooking at 30 rpm, but not mixed in the end-of-cook liquor
- MIX, MIX170 or D: Pulp was mixed in the end-of-cook liquor at 170°C
- MIX100: Pulp was mixed in the end-of-cook liquor at 100°C
- MIX130: Pulp was mixed in the end-of-cook liquor at 130°C
- +14: Bauer McNett +14 long fiber fractions from the pulp
- RW: pulp cooked from round wood chips
- SC: pulp cooked from saw mill chips

4 RESULTS AND DISCUSSION

The main results of the study, together with a discussion, are presented in this section. The effect of mechanical treatment on strength properties of softwood kraft pulp is firstly discussed (Publications I and V). Secondly, the effects of mechanical treatment on fiber surface layer properties are discussed (Publication II). The results of the effects of mechanical treatment on fiber and on fiber wall structure are next analyzed (Publication III). Finally, the effects of mechanical treatment on kraft pulps from different raw materials are discussed in relation to the previous findings (Publication IV). Based on this, conclusions relating to the mechanism for fiber strength deterioration are drawn (Publication III).

4.1 Strength properties

Strength properties of a fiber network are the sum of the fiber network properties and the fiber strength. The network properties are therefore affected by both fiber damage and deformations. Pulp sheets made from fibers having dislocated fiber walls, curl and kinks will have enhanced stretch and tear indices compared with pulp sheets prepared from fibers lacking deformations (Kibblewhite 1976, Page et. al.1985). The number of fiber deformations or singularities has also been reported to reduce single fiber strength (Seth 1999a, Mohlin et. al. 1996, Iribarne 1999). Increasing degradation of cellulose chains has also been reported to reduce fiber strength (Gurnagul et.al. 1992).

The results in Figure 6 /I/ compare the tear index and tensile index of mechanically-treated pulps. The tear strength of the DEDED-bleached pulps decreased when they had been subjected to mechanical stress at the end of the cook. A higher temperature during the mechanical treatment led to increased strength loss. When the treatment temperature was 170°C, the tear index at a tensile index of 70 N•m/g decreased dramatically (by approximately 45% compared to the reference). Even slight stirring

during cooking reduced the tear index of the NOMIX pulp by 10% at a tensile index of 70 N•m/g compared to the REF pulp, which had no mechanical treatment.

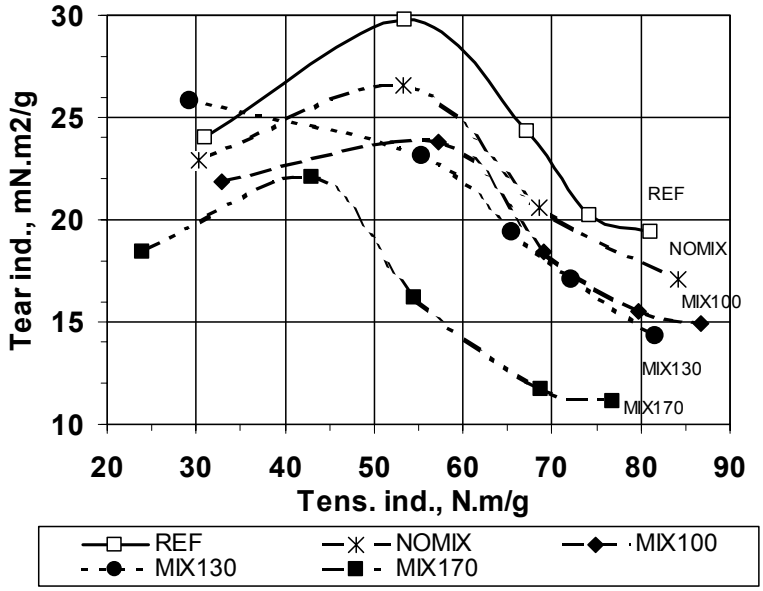

Fig. 6. The effect of mechanical treatment on tear index as a function of tensile index of the DEDED-bleached pulps /I/.

Fiber strength was also measured by the zero-span tensile index (wet) method. The results, presented in Fig. 7 /I/, show clearly that the zero-span tensile index as a function of tensile index decreased when the mixing temperature was increased, although this phenomenon was not as clear as with the tear index measurement.

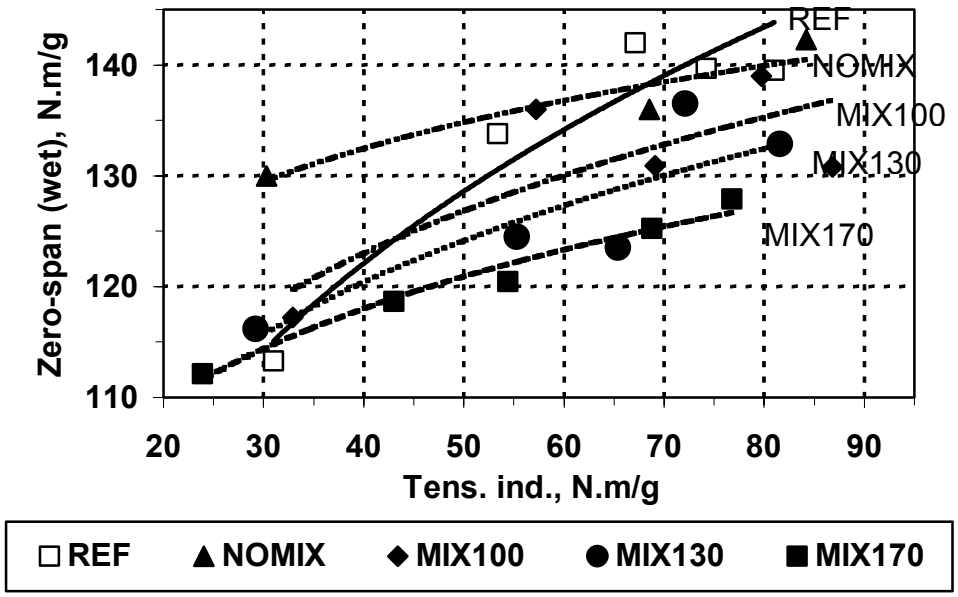

Fig 7. The effect of mechanical treatment on zero-span tensile index (wet) as a function of tensile index of the DEDED-bleached pulps/I/.

Very clear correlations have been shown between the number of fiber deformations (curl, kinks and twist) and zero-span tensile index. Results reported in the literature suggest that zero-span should be measured for well-beaten (2000-4000 PFI revolutions) straight fibers (Mohlin et. al. 1996, Seth 1999a, Clark 1997). Our results, however, are in disagreement with this. The number of fiber deformations (curl, kinks and dislocations) were measured for the MIX and NOMIX pulps which gave the highest differences in the tear index and zero-span tensile strength results. The results are shown in Table 1 /I/.

Table 1. Fiber damage measured for DEDED-bleached NOMIX and MIX pulps. 0=no beating, 1000 and 2000 = PFI beating to 1000 and 2000 revolutions /I/.

	NOMIX 0	NOMIX 1000	MIX 0	MIX 1000	MIX 2000
Degree of dislocation	2.50	2.60	2.50	2.60	2.90
Curl index	0.40	0.30	0.56	0.35	0.17
Fiber length, l.w. average, mm	2.59	2.88	2.74	2.78	2.65
Kinks, number of kinks /mm	0.28	0.20	0.31	0.25	0.07
Tensile index, N·m/g	30.3	68.5	23.9	54.4	68.8

The results in Table 1 show that the number of fiber deformations decreases as a function of PFI revolutions for both pulps, but there is no clear correlation between the zero-span tensile strength values (shown in Fig. 7) and the number of fiber deformations.

If the pulp strength is evaluated when the fibers are near the same fiber deformation level (MIX had slightly more fiber deformations), which would in this case be after 1000 PFI revolutions, the results show that the zero-span tensile strength is lower for the MIX pulp. However, if the fiber strength of these two pulps were the same, the fiber network having the greater number of fiber deformations (MIX pulp), should give a higher tear index, because fiber deformations enhance tear index (Page et. al. 1985, Van den Akker 1944). However, Fig. 6 shows that the tear index for the MIX pulp was significantly lower than that for the NOMIX pulp. In addition, the large number of fiber deformations reduces the tensile index because of the nonuniform stress transfer in the fiber network (Page et. al. 1985). The strengths of these two pulps can also be evaluated at the same tensile index level 68 Nm/g (Table 1 and Figs. 6 and 7) at which the number of deformations is lower for the MIX pulp than for the NOMIX pulp. This comparison strongly suggests that the fiber strength of the MIX pulp is significantly reduced as a result of mechanical treatment. The effect of fiber deformations on single fiber strength and fiber network properties is discussed in more detail below.

4.1.1 Fiber deformations

The effects of fiber deformations on single fiber strength and fiber network properties were studied by introducing deformations into the unbleached fibers without reducing fiber strength or changing fiber swelling. The deformations were gently introduced and the unbleached pulps were beaten in a PFI beater to 2000 revs. Spruce RW (RW=round wood) kraft pulp fibers were used in this part of the study (Publication V). Figs 8 and 9 show fiber curl and kinks after 0, 15 and 45 minutes' treatment time in the mixer.

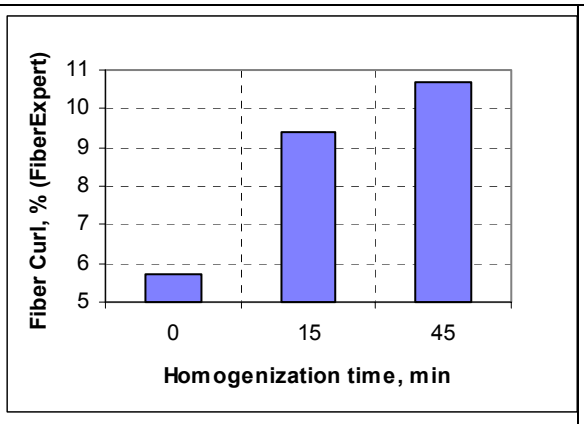

Fig. 8. The development of fiber curl as a function of mixing time for unbleached pulps /V/.

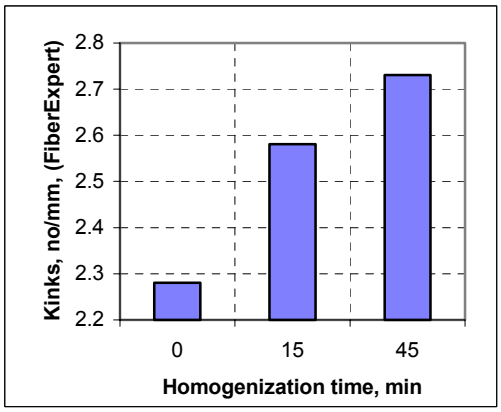

Fig. 9. The development of fiber kinks as a function of mixing time for unbleached pulps /V/.

Figs. 8 and 9 show that mixing in the Hobart mixer increased fiber curl and the number of kinks in the fibers. Figs. 10 and 11 show tensile stiffness index and tensile

index as a function of fiber curl. The graphs show that when the number of fiber deformations increased, the pulp sheet tensile index and stiffness decreased. This phenomenon can be explained by the deformed fibers (ie. fibers with curl and kinks) forming a network in which the load distribution is non-uniform (fiber segment activation is not uniform) compared to a network formed from straight and undeformed fibers. The non-uniform load distribution results in local stress concentration points which break when the fiber network is drawn, resulting in low tensile index values. The stretch increases in such a fiber network because of the slack fiber segments which have to be straightened before they are able to carry load, compared to a fiber network of straight fibers.

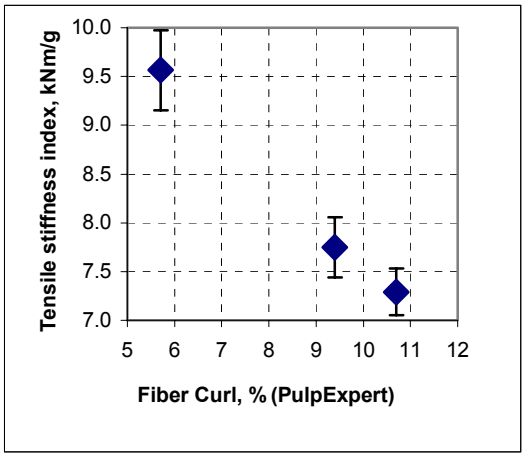

Fig. 10. The development of tensile stiffness index as a function of fiber curl for unbleached pulps. Error bars 95% confidence interval of the mean of the measurement /V/.

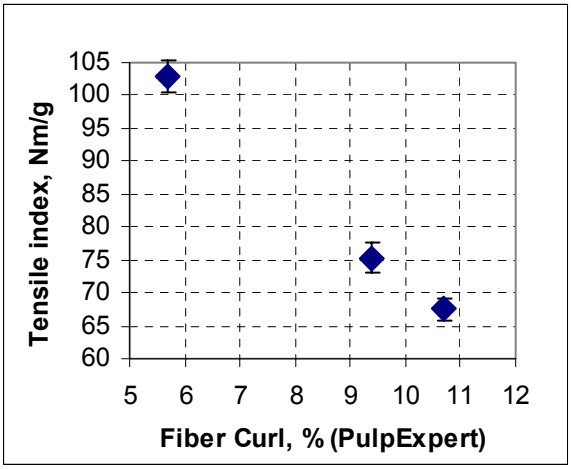

Fig. 11. Tensile index of the pulp sheet as a function of fiber curl for unbleached pulps. Error bars 95% confidence interval of the mean of the measurement /V/.

The decreases in tensile properties of the pulp sheet cannot be explained by differences in fiber bonding (Scott Bond), because they are quite small (Fig. 12).

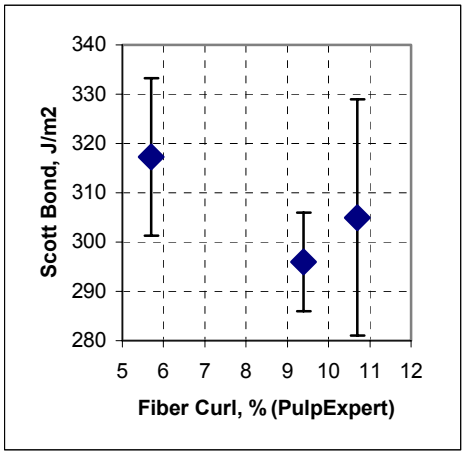

Fig. 12. The development of Scott Bond as a function of fiber curl for unbleached pulps. Error bars 95% confidence interval of the mean of the measurement /V/.

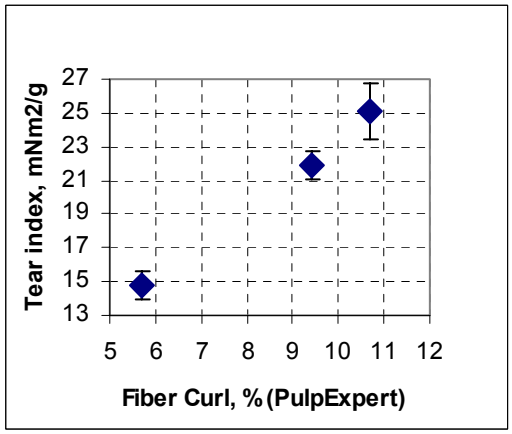

Fig. 13. The development of tear index as a function of fiber curl for unbleached pulps. Error bars 95% confidence interval of the mean of the measurement /V/.

From Fig. 13 it may be concluded that the tear index increases when the fibers in the fiber network are deformed. The deformed fibers therefore transfer stresses to a larger area and to more bonds, which in breaking consume greater energy which is seen as higher tear indices. However, Fig. 14 shows clearly that the deformation process (homogenization) did not affect single fiber strength. The zero-span tensile (wet) index results were approximately the same. It may also be concluded from Fig. 14 that fiber curliness has no effect on the zero-span (wet) tensile measurement. The zero-span result, therefore, is an indicator of average single fiber strength.

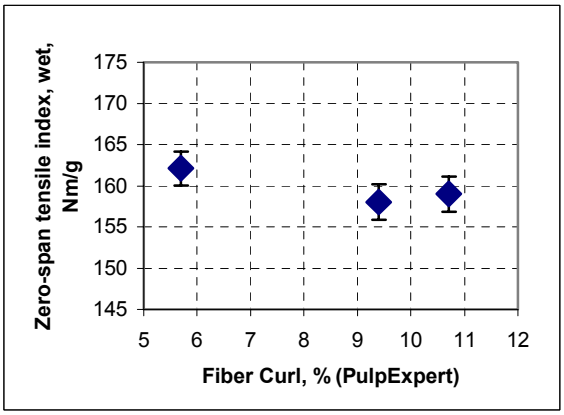

Fig. 14. The development of zero-span index as a function of fiber curl for unbleached pulps. Error bars 95% confidence interval of the mean of the measurement /V/.

According to the literature (Seth 1999a, Mohlin et. al. 1996) the zero-span fiber strength should be measured for well-beaten, straight fibers. This recommendation is mainly based on the hypothesis that curly fibers do not carry load in the measurement

and they have to be beaten to be straightened. The explanation for this difference could be that the fibers with mechanically or chemically modified fiber walls distribute load non-uniformly within the fiber wall. This means that very carefully handled fibers having no damage to their walls can therefore transfer more load, regardless of the degree of fiber deformation compared to damaged fibers.

It has been reported that the zero-span measurement is dependent on the measurement technique in which the pulps sheets are rewetted. According to the hypothesis of Gurnagul and Page (1992), the weakening of the sheets by wetting is dependent on the chemical and mechanical treatment that the pulp has received. Gurnagul and Page also hypothesize that the mechanical treatment might weaken the lignin-hemicellulose matrix, causing chemical differences that allow the fibrils to slide over one other, thereby reducing wet fiber strength. The fiber strength and the effects of carbohydrate composition and pulp viscosity on the strength properties are discussed below.

4.1.2 Microscopic damage analysis

The NOMIX and MIX DEDED-bleached pulp sheets were tested using in-plain tear testing and damage analysis techniques /I/ developed by Kettunen and Niskanen (2000a). The damage analysis gives ‘the damage width’, which is the size of the damage zone (fracture process zone) of the pulp sheet. In Fig. 15 tearing work index and damage width are compared.

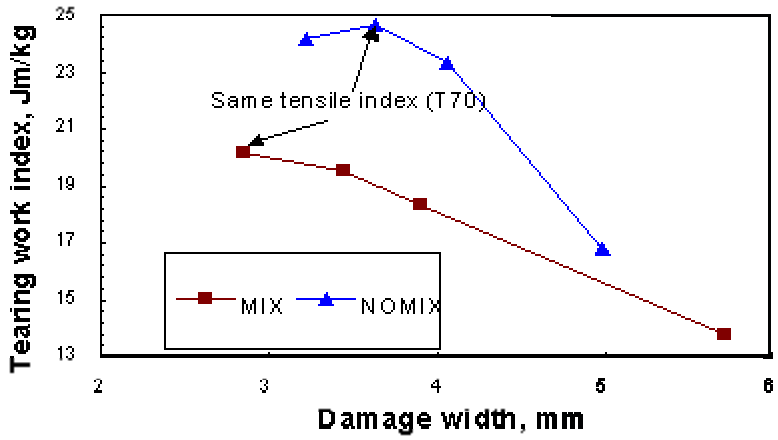

Fig. 15. Tearing work index as a function of damage width for DEDED-bleached NOMIX and MIX pulps /I/.

Fig. 15 shows that the damage width of the MIX pulp was approximately 1mm smaller, and less tearing work was required to break the sample made from the MIX fibers than that made from the NOMIX fibers at the same tensile index. This indicates that the proportion of broken fibers (compared to fibers pulled-out as whole) in the MIX pulp was larger than in the NOMIX pulp. This suggests, therefore, that the strength of a single fiber was lower for the MIX than for the NOMIX pulp. The reduced damage width at the same tensile index confirms this.

4.1.3 Fiber length

Most of the tear-related strength properties of a fiber network have been attributed to fiber length. According to Niskanen (2001) fiber length has a large effect, for example, on the in-plane fracture energy and, according to Hiltunen (2003), when fiber strength is not low the fiber length seems to be more important than strength. The effect of fiber length on fiber network strength was studied by fractionating the DEDED bleached NOMIX and MIX pulps to long-fiber fractions (+14 fraction) and comparing the properties of these to those of the whole pulp (Fig. 16) /I/.

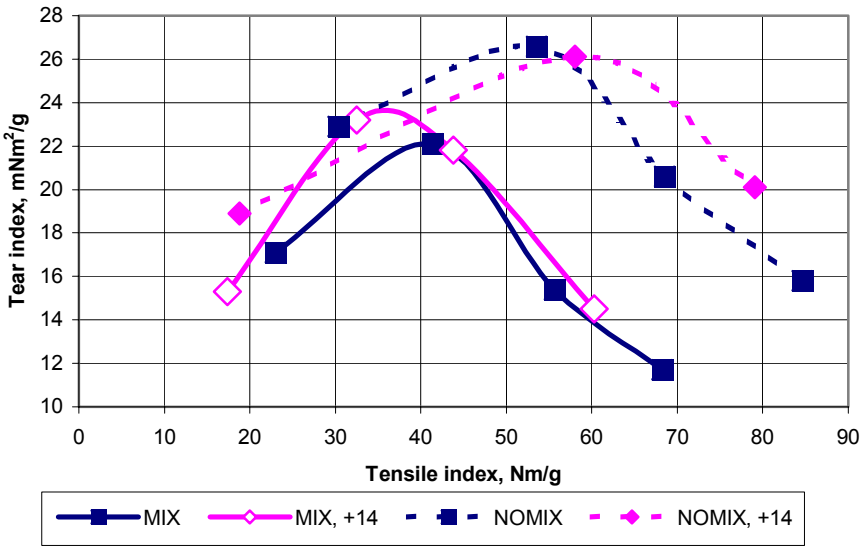

Fig. 16. Tear index as a function of tensile index for bleached NOMIX and MIX170 pulps and Bauer McNett +14 fractions (PFI beating) /I/.

The tear index of the long-fiber fraction (+14 fraction) of the NOMIX pulp was higher than that of the whole pulp at the same tensile index (Fig. 16). The long-fiber fraction of the MIX pulp, however, had the same tear index as the corresponding bulk pulp. This indicated that even though the longer fibers in the +14 fraction (length weighted average fiber length approximately 3.3 mm for the +14 fraction) should have given a higher tear index, this did not compensate for the lost single fiber strength. This confirms the results from the microscopic damage analysis indicating that the loss in strength originated in the loss of single fiber strength rather than in fiber-fiber bonding ability.

4.1.4 Carbohydrate composition and pulp viscosity

The intrinsic viscosity of pulp is used as an indication of cellulose chain length, molar mass (M_w) or degree of polymerization, which in turn have been related to fiber strength of cellulosic fibers (Page et. al.1985, Gurnagul et.al 1992, Berggren 2003). The fiber strength decrease via cellulose degradation has been attributed to two different kinds of cellulose degradation patterns, homogeneous (e.g. alkaline degradation) or heterogeneous (acid hydrolysis) degradation. The effect of homogeneous (alkaline) degradation is seen on pulp strength properties only at low viscosity values, below 600 ml/g (Berggren 2003). Heterogeneous cellulose degradation causes local weak points in the fiber cell wall, which result in low fiber strength values at high intrinsic viscosity values (Gurnalgul et.al. 1992, Berggren 2003). Mechanical treatment of kraft pulps, both laboratory and mill pulps, has been reported to have no effect on their intrinsic viscosity values (Bennington 1989, Clark et. al. 1997, Seth 1999b, Iribarne 1999). Our results show practically no difference between the NOMIX and MIX pulps with respect to the carbohydrate composition and intrinsic viscosity. The concentrations and types of monosaccharides detected by liquid chromatography following acid hydrolysis of the bleached and intrinsic viscosity measurements of the unbleached pulps are shown in Table 2 /I/. The results show that there was little or no difference in the concentration and types of monosaccharides between the bleached NOMIX and MIX pulps. It may be assumed, therefore, that the strength loss was not due to measurable changes in carbohydrate composition.

Table 2. Viscosities of MIX and NOMIX pulps at kappa number 27 (calculated using 1 kappa unit≈16 ml/g). The carbohydrate composition of the bleached pulps was detected as monosaccharides after acid hydrolysis /I/.

PULP	VISCOSITY, at kappa umber 27	MONOSACCHARIDES AFTER ACID HYDROLYSIS, %				
	ml/g	Arabinose	Galactose	Glucose	Xylose	Mannose
NOMIX	1250	0.7	+	84.9	8.1	6.3
MIX	1260	0.7	0.3	84.9	7.9	6.2

It has been suggested that differences in the cellulose polymorphs of cellulose microfibrils might influence the strength properties of cellulosic fibers (Ishikawa 1997 and Hsieh 2000) for cotton and ramie, for example. According to Liitiä (2000), in pulping part of the cellulose I_α is converted to the more stable form I_β, and this is mainly induced by heat. Table 3 shows the results obtained from solid state NMR measurements to determine whether the mechanical treatment during pulping had induced differences in cellulose polymorphs between the pulps. The study was carried out using unbleached and unbeaten fibers.

Table 3. The results of solid state NMR analysis of unbleached and unbeaten MIX and NOMIX fibers /II/.

SAMPLE	DEGREE OF CRYSTALLINITY, %	CELLULOSE I_α, %	CELLULOSE I_B, %
NOMIX	52	27	73
MIX	53	25	75

Table 3 shows that the mechanical treatment did not change the degree of crystallinity or the number of different polymorphs. Mechanical treatment in pulping did not affect the degree of conversion of cellulose I_α to I_β. Therefore, differences in the crystallinity or relative fractions of cellulose I_α to I_β do not appear to be a factor in the higher strength of the NOMIX relative to the MIX pulp.

It may be concluded from fiber deformation measurements that the number of fiber deformations increased following mechanical treatment at room temperature of kraft pulp fibers after cooking. The increase in number of fiber deformations did not reduce single fiber strength but did affect the strength properties of the fiber network. The strength loss of the MIX pulp could not be shown to be due to measurable changes in carbohydrate composition or differences in the crystallinity or relative fractions of cellulose I_α to I_β. The effects of mechanical treatment on fiber bonding and on properties of the fiber surface layer are discussed below.

4.2 Fiber bonding and fiber surface layer

Pulp sheet strength properties are also affected by interfiber bonding which transfers the stresses in the fiber network. Fiber bonding ability is developed during chemical and mechanical treatments, and is a combined effect of both these treatments on the fibers and fiber surfaces (Paavilainen 1993). The parameters that influence bonding are reported to be: fines content (Panula-Ontto 2003); fiber dimensions and relative bonded area, which is dependent on the swelling of the wet fibers; and fiber flexibility (Paavilainen 1993). Usually WRV is considered to be a measure of fiber swelling and therefore it seems appropriate to relate WRV to properties influenced by fiber flexibility (ie. tensile index and Scott bond) (Paavilainen 1993). The bonding ability of softwood fibers can be altered by changing either the bonding strength or the bonded area. Usually the bonding strength is a function of the strength of elementary bonds and their number per unit bonded area. The bonded area is affected by fiber conformability (flexibility and fiber collapsibility). Fiber conformability is not a directly measurable quantity but a general term that characterizes fiber behavior in the web consolidation process. Conformable fibers can bend and match the shape of each other to give a dense and well bonded fiber network. In this study only the effect of mechanical treatment on the fiber surface layer and on the bonding ability is discussed /II/. The bonding ability is characterized using the Scott bond measurement.

4.2.1 Fiber bonding

In this study the interfiber bonding is related to the z-directional strength of the pulp sheet. The Scott bond measurement was used to measure and describe the bonding strength between fibers. The Scott bond values of the MIX pulp at a given tensile index (measured for both unbleached and bleached MIX and NOMIX pulps) were slightly higher than those of the NOMIX pulp. At 0 PFI revolutions the Scott bond value of the MIX pulp was the same as or even slightly higher than that of the NOMIX pulp and the WRV value was lower for the former (Table 4) /II/.

Table 4. PFI revolutions, tensile index water retention value (WRV) and Scott Bond at tensile indices of 50 N•m/g (T50) and 70N•m/g (T70) measured for MIX and NOMIX, unbleached and bleached pulps /II/.

	UNBLEACHED		BLEACHED	
Analysis	MIX	NOMIX	MIX	NOMIX
PFI revs. to T50	1047	0	659	425
PFI revs to T70	-	550	1922	1093
Tensile index Nm/g @0 PFI revs.	23.1	51.7	21.1	30.3
Scott Bond, J/m^2@0 PFI revs.	84	71	158	149
Scott Bond, J/m^2@T50	149	71	222	-
Scott Bond, J/m^2@T70	210	221	307	271
Unbleached WRV, g/g (unbeaten)	1.5	1.8	-	-

Figure 17 shows the Scott bond as a function of PFI beating revolutions measured for mechanically damaged and undamaged pulps prepared from the different raw materials.

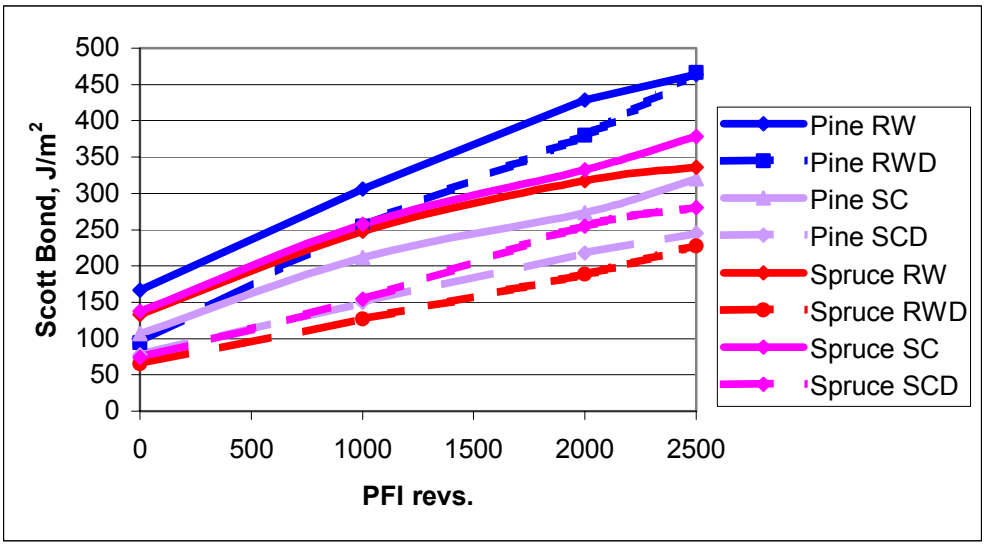

Fig. 17. Scott bond as a function of PFI beating revolutions measured for unbleached mechanically treated and untreated pulps prepared from the different raw materials /IV/.

It may be concluded from the results shown in Table 4 and Fig. 17 that the mechanical treatment of kraft fibers decreased the z-directional bonding strength (Scott bond) of the pulp sheet. When the bonding strength comparison is done at the same the tensile index level, the mechanically-treated pulps gave higher Scott bond values because of the higher beating level /IV/. From Fig. 17 it can be further concluded that the decrease in z- directional bonding strength could be an indication of homogenous deterioration of the fiber surface layer.

The damaged fibers had a much greater number of deformations, especially fiber curl /IV/. The high fiber curl could enhance the formation of a felted sheet structure. Such a structure (higher fiber entanglement) should give better z-directional strength than layered structures, because fibers are stronger than bonds. Therefore, it might be expected that the mechanically-treated fibers, despite their lower flexibility, would have given at least the same or even higher Scott bond values.

Other factors affecting fiber bonding (e.g. fines content and degree of fibrillation) were measured for both NOMIX and MIX pulps. An increase in fines content has been reported to enhance bonding in the pulp sheet structure (Paavilainen 1993). The fines content of bleached MIX and NOMIX pulps was measured using a DDJ (unbeaten), and a Kajaani FS-200 instrument but no differences were detected between the pulps. The fibrillation of the outer fiber wall during the mixing treatment might enhance fiber bonding. The degree of fibrillation of the bleached MIX and NOMIX pulps is shown in Table 5.

Table 5. The degree of fibrillation of the bleached MIX (after 0, 2000 PFI revs.) and NOMIX pulps (after 0, 1000 PFI revs). (1000 and 2000 PFI revs present approx. the same tensile level) /II/.

PFI REVS	MIX			NOMIX		
	Low fibril.	High fibril.	Broken	Low fibril.	High fibril.	Broken
0	80%	13%	7%	82%	13%	5%
1000	-	-	-	64%	29%	7%
2000	53 %	40 %	7%	-	-	-

The degree of fibrillation of the bleached, unbeaten MIX and NOMIX pulps was the same (Table 5), which meant that the mechanical treatment did not fibrillate the outer fiber surface. Table 5 also shows that the MIX pulp was more fibrillated after 2000 PFI revolutions than the NOMIX pulp after 1000 PFI revolutions (same tensile index). The fiber surfaces of the MIX and NOMIX pulps were subsequently studied more closely in order to find explanations for the different behavior of the fibers.

4.2.2 Fiber surface layer

The fiber surface layer is very important in bond formation between fibers. The bonding between fibers is conventionally considered to be primarily due to hydrogen bonding, but van der Waals forces are also considered to be important. The surfaces between these bonds have to be in close proximity to enhance bonding. For hydrogen bonding this distance is approximately 0.17 nm and for van der Waals forces it is between 0.3 and 0.5 nm. Any irregularity on these binding surfaces reduces the bonding area, which in turn decreases the bonding strength. The bonding ability of the NOMIX and MIX fiber surfaces was measured as the contact ratio of wet fibers using glass as the contact surface. The results from these measurements are presented in Table 6 /II/.

Table 6. Contact ratios of the unbleached, unbeaten MIX and NOMIX pulps /II/.

RUN NUM.	1.	2.	3.	4.	5.	AVERAGE VALUE
NOMIX	45.6	43.6	31.6	57.6	36.4	43
MIX	15.3	23.3	20.8	19.5	22.7	20

Table 6 /II/ shows that the contact ratio of the MIX pulp was approximately 45 % lower than that of the NOMIX pulp. It might therefore be expected that the Scott Bond values of the unbeaten unbleached and bleached pulps would be lower for the MIX pulp. Scott bond values, however, were the same or slightly higher for the unbeaten MIX than NOMIX pulps (Table 4 /II/). One possible reason for this unexpected result could be that the contact ratio measurement was affected by the different levels of curl and other fiber deformations, which enhanced fiber entanglement.

A pulp with a higher contact ratio should have a higher tensile index, as was the case for the NOMIX and MIX pulps. A reason for the differences in the contact ratio measurement could be that the pulps dried differently on the glass surface. For example, deformed fibers (MIX pulp) shrank in such a way that the surface contact vanished. Another explanation for this phenomenon could be that the macrofibrils or fibril aggregates of the MIX pulp, which could have been separated from each other, formed a less uniform surface layer than did the NOMIX pulp fibers. The separation of the structural elements in the fiber surface layer could reduce the contact ratio and decrease bonding after beating via structural weaknesses. This hypothesis was studied using Atomic Force Microscopy (AFM) and immunolabeling (surface accessibility) of the fibers.

AFM was used to study the surface differences between the fibers of the unbleached unbeaten MIX and NOMIX pulps. The fibers were imaged in tapping mode to capture dual height and phase images. The gray-value distributions of the phase images indicated more irregularities on the surface layer of the MIX fibers than of the NOMIX fibers /II/. The problem with AFM is that the area of interest is so small that it can lead to incorrect conclusions.

The immunolabeling (surface accessibility) study using antibodies specific to xylan or lignin, indicated that the area of labeling of the unbleached MIX pulp fibers was slightly larger, and the labeling more intense, than for the fibers of the unbleached NOMIX pulp. One interpretation could be that there was more antibody associated with the surface areas of the mixed fibers than the unmixed fibers, indicating that the surface of a mixed fiber was more accessible to labeling /II/. An explanation for this phenomenon could be that the fiber surface or wall of the MIX pulp fibers had opened up in such a way that the macrofibrils or fibril aggregates had separated from each other to enhance the attachment of the antibodies.

4.2.3 Fiber Charge

Certain chemical groups, such as carboxylic acid groups, dissociate in water promoting fiber swelling and contributing to improved fiber flexibility and fiber wall conformability. Generally, the degree of swelling of polyelectrolyte gels increases with increasing charge density of the gel network, and decreases with increasing cross-linking, ionic strength or valency of counter ions (Lindström 1992). Laine (1996) has shown that water retention and fiber flexibility increase as the charge of the bleached softwood fibers increases. The plasticization of the cell wall (i.e. the penetration of water) causes debonding and the separation of solid elements (microfibrills, lamellae), and increases with the degree of swelling (Emerton 1957, Scallan 1983). This plasticization loosens the cell wall structure and affects the flexibility of the fibers. Increased fiber charge, therefore, promotes fiber bonding (Laine 1996).

Because the swelling (WRV value) of the fibers decreased as a result of mechanical treatment, fiber charge was measured for the unbleached and unbeaten MIX and NOMIX pulps. Table 7 shows total charge of the fibers measured with magnesium elution method according to Sjöström (1961) and surface charge with adsorption of poly (dimethyldiallylammonium) chloride /II/.

Table 7. Total charge measured as carboxylic acid units and surface charge /II/ measured for unbleached and unbeaten NOMIX and MIX pulps.

SAMPLE	TOTAL CHARGE, mmol/kg FIBER (carboxylic acids)	SURFACE CHARGE (TITRATED FROM FIBER SUSPENSION), μeq/g FIBER
NOMIX	105	-25.3
MIX	95	-25.9

Table 7 /II/ shows that there were no such differences in the charge results, which could explain the decrease in the WRV-value of the mechanically-treated (MIX) fiber (Table 4.).

The AFM and immunolabeling results, together with contact ratio measurements, support the hypothesis of separation of the structural elements on the fiber surface layer. The separation of structural elements might enhance the irregularities on the fiber surface layer so reducing the bonding area. The bulking of the fiber surface layer (e.g. more separated layers) might reduce the ability to resist z-directional stresses. Both the surface irregularities and the separation of structural elements on the fiber surface might explain the lower Scott bond values of the mechanically-treated fibers.

4.3 The fiber wall ultrastructure and strength properties

The 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, fiber swelling affects fiber conformability and flexibility, which in turn affect the strength properties of the fiber network (Paavilainen 1993). That beating increases fiber swelling has been attributed to internal fibrillation of the fiber wall. Increased fiber swelling increases the drying stresses which is reported to be beneficial, to the tensile index and elastic modulus of the fiber network when fiber network is restrained dried (Htun 1980). Gierz (1979) has argued that the increase in tensile strength during restrained drying is caused by increased fiber segment activation. During drying fibers shrink and through the microcompression effect create drying stresses in the network. These stresses straighten slack fiber segments enabling them to carry load so that the load carrying capacity of the whole fiber network increases. Van der Akker (1966) suggested that the increase in fiber swelling after beating might increase the axial elastic modulus of fibers via the ‘Jentzen effect’. Jentzen (1964) has shown that when single fibers are dried under strain their elastic modulus increases. This increase in the elastic modulus contributes to the

rearrangement of the fiber wall constituents. The drying tension straightens the fibers, pulls out dislocations and other defects and reduces fibril angle. Changes may also occur at the molecular level where the cellulose and hemicellulose chains may rearrange and align parallel to the external load. The swollen state of the fiber cell wall matrix is necessary for the structural and molecular rearrangement of the fiber wall during drying. For example, Lindström (1986) reported a number of correlations between the swelling values prior to sheet forming and the tensile or burst strength of dried pulp sheets.

The fiber wall pore structure and the fibril aggregate size distribution during kraft pulping has also been shown to affect the strength properties of kraft pulp (Andreasson 2003).

It was suspected that the differences between NOMIX and MIX pulps with respect to fiber strength properties was related to fiber wall structure /III/. Water retention, surface area and cell wall thickness measurements were therefore used to determine whether there were changes in the fiber wall pore structures that might explain the differences in water retention.

The water retention value of MIX and NOMIX fibers was measured as a function of g-force, to provide an indication of the nature of the change in the fiber wall pore structure. The results of the water retention values of unbleached MIX and NOMIX pulps after centrifuging at different g-forces are presented in Table 8 /III/.

Table 8. The results of the water retention values of unbleached and unbeaten MIX and NOMIX pulps at different g-forces /III/.

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 8 /III/ show that the water retention value of the MIX pulp fibers was lower than that of the NOMIX fibers at all g-forces. There was a significant difference in water retention between NOMIX and MIX pulps at different g-force levels. A possible explanation for the difference could be that the MIX pulp fibers were less swollen (i.e. they had lost their swelling ability) than the NOMIX fibers. The water retention of fibers describes the swelling of the fiber wall (Lindström 1992, Scallan et. al. 1972). However, WRV measurements may not be appropriate 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 (Scallan et. al. 1972). This might have been the case in our study.

The fiber wall structure was also studied using nitrogen adsorption (BET). This technique gives the surface area of the sample, which correlates linearly with fiber wall pore volume (Stone and Scallan 1965). The surface areas of the unbleached MIX and NOMIX pulp fibers were measured for liquid exchanged and CPD (critical point drying) dried fibers /III/. The results indicated no differences in surface area between the samples. This suggested that there should be no differences in pore volume between the samples. Because of the smaller WRV, possibly due to the more 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 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 they were outside the range of the nitrogen adsorption volumetric measurement.

The BET results indicated that there were no differences in fiber wall structure, although there were large differences in the WRV of the pulps. The WRV values of different raw materials for mechanically-treated and untreated fibers and their cell wall thickness indices were measured using a Kajaani FiberLab/IV/. The results are shown in Fig 18.

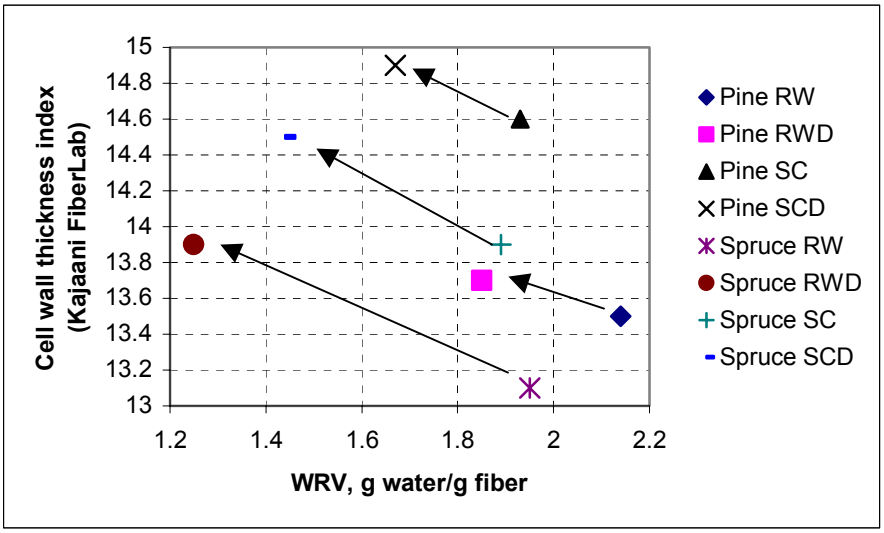

Fig. 18. Fiber cell wall thickness indices of unbleached and unbeaten, mechanically-damaged and undamaged fibers as a function of water retention value /IV/.

Results for the water retention values of the different raw materials (Fig. 18 /IV/) suggest that when the mechanically damaged fibers are subjected to an applied g-force, the fiber wall cannot retain the water within it. The corresponding cell wall thickness indices suggest that when no g-force is applied and the fibers are in wet state, the outer dimensions of the fiber wall remain the same. This result in this case indicates that the water retention value is an indicator of the ability of the fiber wall pore structure to hold water inside the fiber wall at certain g-force, rather than swelling (i.e. structural changes in the fiber wall structure). This holds true if swelling

is considered to be a phenomenon in which the fiber wall dimensions increase. The effect of spindrying, for example, on cell wall thickness via pore closure (Maloney 2000) can be neglected because the pulps were maintained at all times in a water-swollen state at a consistency below 10%.

Because of the inconsistency in the WRV, BET and cell wall thickness index results, the accessibility of the MIX and NOMIX fibers was studied using the solute exclusion technique, thermoporosimetry (Differential Scanning Calorimetry (DSC)) and Simons' staining.

4.3.1 Fiber wall accessibility

The structural changes in the fiber wall resulting from mechanical treatment were studied using Simons' staining and 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. Table 9 /III/ shows how NOMIX and MIX pulps were affected by Simons' stain.

Table 9. The results of Simons' staining (orange, molar mass >25000; blue, molar mass 998) treatment of DEDED-bleached NOMIX and MIX pulps /III/.

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 9 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) as a result of the mechanical treatment.

The solute exclusion method using Dalton dextrans of molecular weight $2x10^6$ was used to determine the Fiber Saturation Point (FSP) of the unbleached and bleached MIX and NOMIX pulps. The advantage of this 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. According to Stone and Scallan (1965), macropores 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 (2000) as micropores. The micropores hold two fractions of water: non-freezing water (NFW) and freezing bound water (FBW) (Maloney 2000). 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 10 /III/.

Table 10. Fiber saturation point value (FSP), freezing bound water (FBW) and non-freezing water (NFW) values for unbleached and belached 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 /III/.

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 10 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 might 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 than 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 wall chemical structures.

The Simons' stained fibers were also embedded into resin to confirm that the stain had reached the fiber wall. Figure 19 shows examples of light micrographs of cross-sections of Simons' stained unbleached MIX fibers (left) and NOMIX fibers (right).

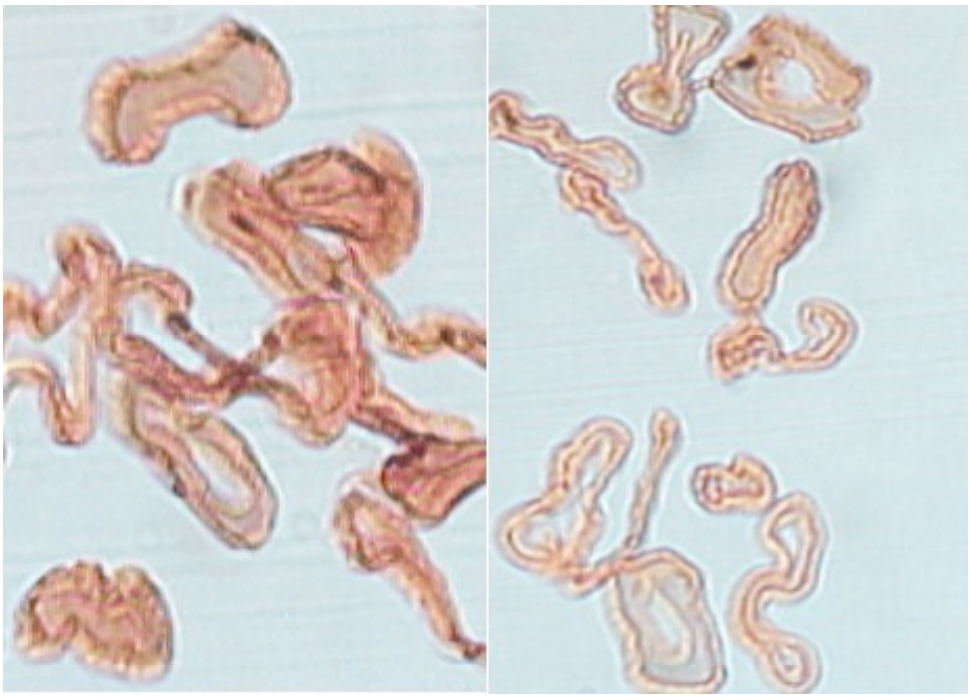

Fig. 19. Light micrographs of cross-sections of Simons' stained unbleached MIX fibers (left) and NOMIX (right) /III/.

Figure 19 /III/ 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 the fiber wall.

A possible explanation for the lower WRV values of the MIX fibers (Table 8) 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 may not have held 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, 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 fibril aggregates) in the fibril (aggregate) skeleton of the fiber wall decreased. The reduced contact between these cellulosic components 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.

4.4 Effect of raw material on fiber damage and deformations

Pine and spruce softwood fibers are different in their cell wall structures. If it is assumed that the fiber wall structure affects fiber strength, then mechanical treatment will have different effects on different fiber wall structures. The average cell wall thickness is slightly higher for pine than for spruce, both for early- and latewood fibers (Johansen 1940). The slightly higher average density and thicker cell wall of pine fibers indicates that there are structural differences in the cell walls between pine and spruce fibers.

The deformation and sensitivity to damage of pulp made from different softwood raw materials was determined by damage experiments carried out under laboratory conditions. The experimental conditions and details of the pulp preparation are presented in more detail in publication IV. Another goal of the study was to investigate the effects of fiber deformations and damage on the strength properties of fiber networks prepared from different raw materials.

4.4.1 Fiber properties and deformations

The effect of mechanical treatment on fiber curl and fiber kinks as a function PFI beating revolutions was investigated for different raw materials. Fig. 20 /IV/ shows the results for fiber curl, which indicate that the spruce fibers were more curled as a result of mechanical treatment than the pine fibers. Most of the curled fibers were those from spruce round wood. Pine round wood fibers were the least curled following mechanical treatment. The fiber curl of the untreated fibers increased slightly during beating and approached the level of the treated fibers' curl which decreased during beating. The explanation for the increased fiber curl could be that when an unchanged fiber wall structure is beaten, the fiber conformability and flexibility increase, which simultaneously increases fiber curl. In contrast, a damaged fiber wall rearranges, the water uptake increases (swelling occurs) and the damaged and curled fibers straighten. The curl of the damaged pulp made from pine sawmill chips approached a level of 8%; that of the damaged pulp produced from spruce sawmill chips approached 9%.

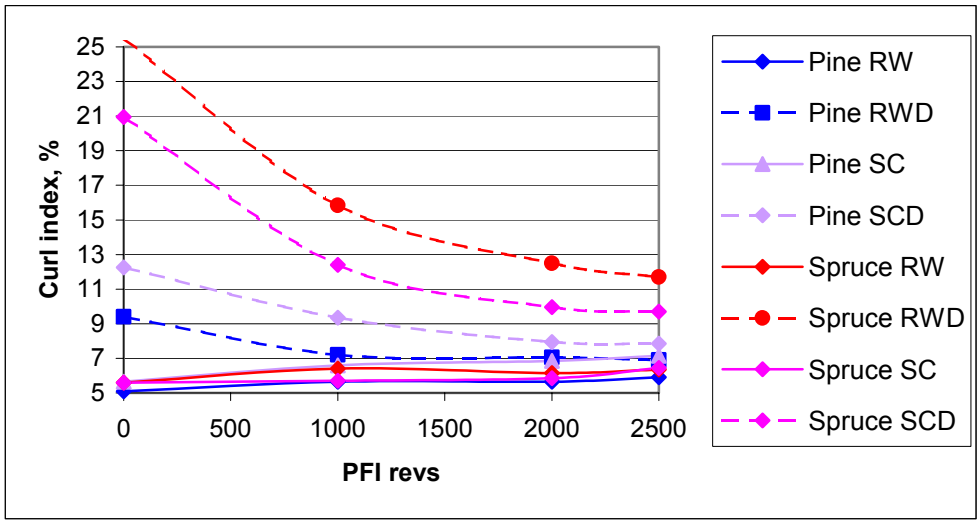

Fig. 20. Fiber curl as a function of PFI revolutions for the unbleached mechanically-treated and untreated pulps. Measured with the FiberExpert /IV/.

Fig. 21 /IV/ shows the fiber kinks results which indicate that the spruce fibers were more kinked as a result of mechanical treatment than the pine fibers. The most kinked fibers were those from spruce round wood. Pine round wood fibers were the least kinked following mechanical treatment. The number of kinks in the untreated fibers decreased slightly during beating.

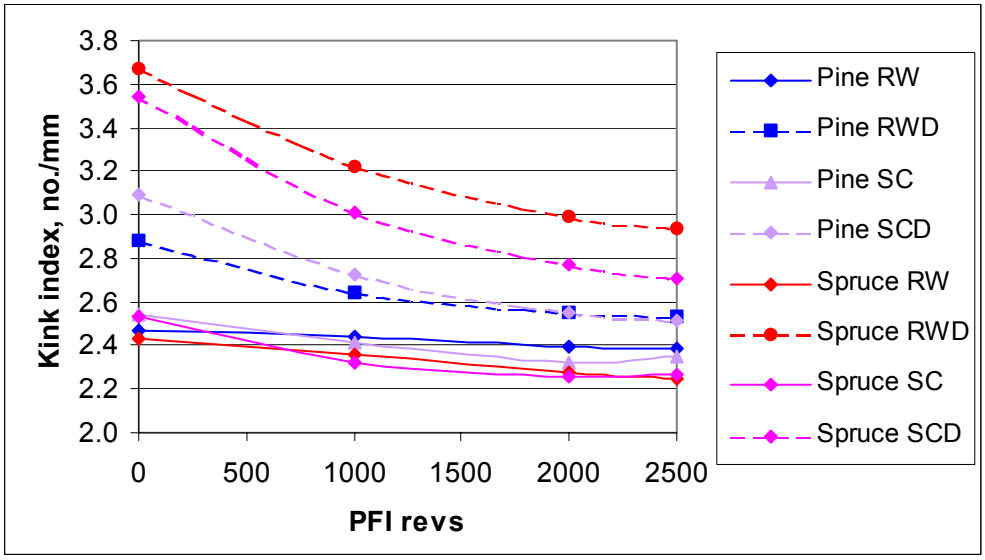

Figure 21. Fiber kink index as a function of PFI revolutions for the unbleached mechanically-treated and untreated pulps. Measured with the FiberExpert /IV/.

Fig. 22 /IV/ shows the WRV results which indicate that the spruce fibers lost more of their ability to retain water as a result of mechanical treatment than did the pine fibers. The spruce round wood fibers exhibited the highest loss of water retaining ability. The results in Figs. 20-22 indicate that the spruce fibers were more deformed and damaged under the same mechanical treatment conditions.

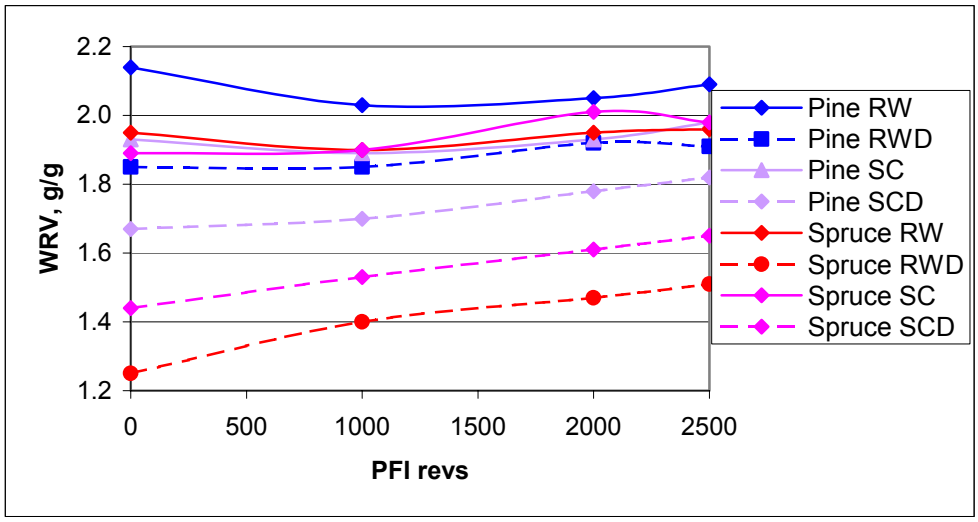

Figure 22. Water retention values as a function of PFI revolutions for the unbleached mechanically-treated and untreated pulps /IV/.

The effect of mechanical treatment on fiber cell wall thickness was also greater for spruce fibers than for the corresponding pine fibers. The fiber wall thickness index of the damaged spruce fibers was slightly higher than that of the corresponding undamaged pulps (Fig. 18 /IV/). One possible explanation for this could be the differences in the fiber wall structure between spruce and pine. The lignin-rich, dense S_1 fiber wall layer of spruce fibers is thinner than that of the corresponding pine fibers (Fengel 1969, Page et. al. 1974). The thicker S_1 layer of the pine fibers might protect the S_2 layer from loosening. Loosening of the S_2 layer of the spruce fibers might be seen as a thicker fiber wall.

4.4.2 Pulp properties and fiber damage

Fig. 23 shows that the tensile index was lower for the unbeaten damaged spruce pulps than for the unbeaten damaged pine pulps. The reason for this was probably that the spruce pulps were much more curled than the pine pulps. The decrease in tensile stiffness and tensile index was probably due to the lower fiber activation, which was shown earlier in Figs. 10 and 11. During drying fibers shrink, and through the microcompression effect (Page and Tydeman 1962) create drying stresses in the fiber network. These stresses straighten slack fiber segments enabling them to carry load more ‘actively’ (Gierz 1979). Niskanen (2000) has suggested that beating affects activation mainly via increased fiber swelling, which then increases the drying stresses during restraint drying. Increased drying stresses straighten fiber segments, that is, they activate them. According to Niskanen (2000) in addition to activation beating also increases the axial elastic modulus of single fiber segments through the Jenzen-effect. As can be seen from Fig. 22 the WRV were lower for the damaged pulps than for the undamaged ones. The results suggest that there was a larger decrease in the WRV of spruce pulps than of pine pulps.

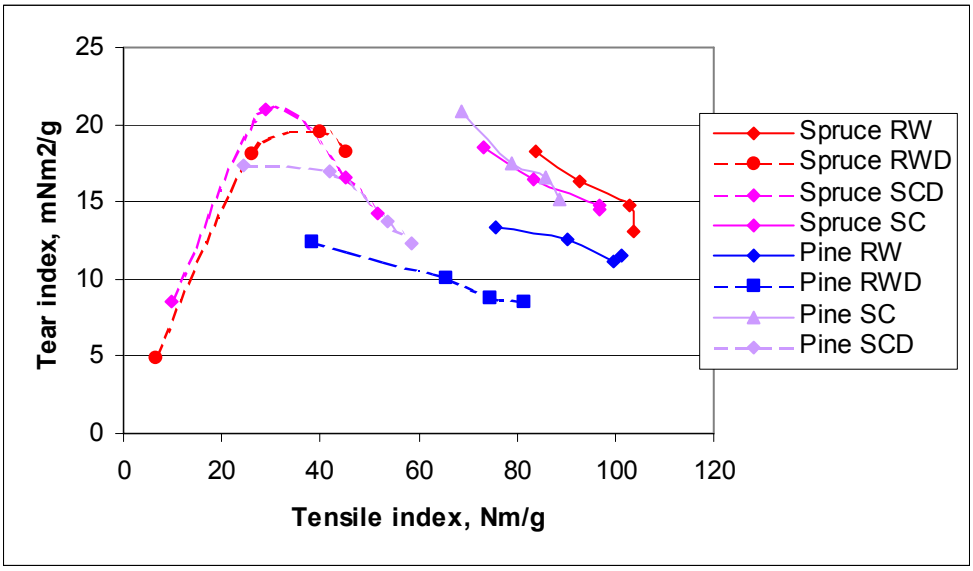

Fig. 23. Tear index as a function of tensile index for the unbleached pulps tested /IV/.

The results shown in Figures 22 and 23 could be interpreted as meaning that the damaged fibers formed a less activated fiber network because of the higher number of fiber deformations and reduced swelling compared to the undeformed fibers (also partly due to lower fiber strength). It is difficult to compare tear index values at a particular tensile index in Fig. 23 because the tensile indices of the undamaged and damaged spruce pulps were at totally different levels. However, there does not appear to be a significant difference in susceptibility to damage between the raw materials tested. When the tear indices of the damaged pulp are extrapolated to the same tensile index level, it can be seen clearly that the strength of the damaged fibers had decreased.

Fiber strength was determined using the wet zero-span tensile values as a function of PFI beating as shown in Fig. 24 /IV/ for the damaged and undamaged pulps. Fig. 24 /IV/ shows that the wet zero-span tensile index decreased more for the spruce pulps than for the pine pulps.

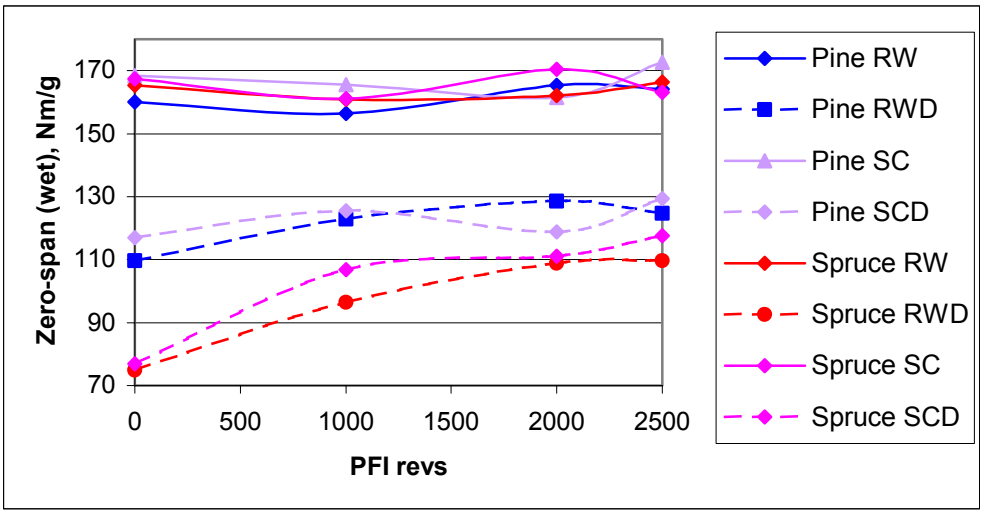

Fig. 24. The Zero-span (wet) fiber strength as a function of beating for the unbleached pulps tested /IV/.

The effect of mechanical treatment on the spruce fibers was more severe than on the corresponding pine fibers. The spruce fibers developed more deformations as a result of mechanical treatment. The decrease in water retention value was also greater for the spruce fibers than for the pine. This, together with the high level of deformation, affected the activation potential (decreased drying stresses) of the spruce fibers in the fiber network and was seen in the very low tensile and tensile stiffness indices /IV/. The treated spruce fibers became weaker than the pine fibers, which was seen in the zero-span results. The bonding of the spruce fibers, measured as Scott bond, was also lower than for the pine fibers (Fig. 17, /IV/). The increase in the cell wall thickness as a result of mechanical treatment was greater for the spruce fibers than for the corresponding pine fibers (Fig. 18 /IV/). The reason for the lower bonding and strength properties could be due to differences in the fiber wall structure between spruce and pine. The lignin-rich, dense S_1 fiber wall layer of spruce fibers is thinner than that of the corresponding pine fibers (Fengel 1969 and Page et. al. 1974). The thicker S_1 layer of the pine fibers might protect the S_2 layer from becoming loose. The loosening of the S_2 layer in the spruce fibers might be seen as a thicker fiber wall and in lower WRV and bonding properties.

Figures 20, 21 and 23 show that the fiber deformations (fiber curl and fiber kinks) were significant in terms of load distribution in the fiber network. The strength of the fiber network is a combination of single fiber strength and the load distribution properties of the network.

5 CONCLUSIONS

The aim of this work was to obtain a better understanding of the effect of mechanical treatment on the properties of softwood kraft pulp fibers, especially fiber strength and fiber network strength properties.

Deformation and damage
Deformations are reversible during beating and affect fiber network properties but not single fiber strength. Damage is partly reversible during beating and reduces single fiber strength.

Effect of damage temperature
It was found that the introduction of mechanical energy at the end of a kraft cook lead to a dramatic drop in pulp strength properties compared to those of pulp which had not been exposed to mechanical treatment. Mechanical treatment, which in this case was mixing (i.e. application of pressing and shear forces) at high temperature and high alkali concentration caused a decrease in strength of the fully bleached pulp. A decrease in temperature during the treatment reduced the strength loss.

Effect of raw material
The effect of mechanical treatment on spruce fibers was more severe than on the corresponding pine fibers. The spruce fibers developed a greater number of deformations as a result of mechanical treatment. The decrease in water retention value was also greater for the spruce fibers than for the pine. This, together with a high level of deformation, affected the activation potential (decreased drying stresses) of the spruce fibers in the network and was seen as very low tensile and tensile stiffness indices /IV/. The treated spruce fibers became weaker than the pine fibers, which was seen in the zero-span results. The increase in cell wall thickness as a result of mixing was also greater for the spruce fibers than for the corresponding pine fibers. The reasons for the lower bonding and strength properties are probably related to differences in the fiber wall structures of spruce and pine. The lignin-rich, dense S_1 fiber wall layer of spruce fibers is thinner than that of the corresponding pine fibers. The thicker S_1 layer of the latter might protect the S_2 layer from becoming loose. The loosening of the S_2 layer in the spruce fibers might be seen as a thicker fiber wall as well as lower water retention values and bonding properties. Fiber deformations (fiber curl and fiber kinks) had a significant effect on the load distribution of the fiber network. The strength of a fiber network results from a combination of single fiber strength and the load distribution properties of the network.

Effect of damage on fiber chemistry and wall structure
The mechanical treatment of kraft pulp increased the number of fiber deformations (curl and kinks). However, during beating the degree of fiber deformity approached the same level in both treated and untreated pulps. At the same degree of fiber

deformity the mechanically-treated fibers were much weaker than the untreated fibers. It could not be demonstrated that strength loss was due to measurable changes in carbohydrate composition or in differences in the crystallinity or in the relative fractions of cellulose I_α to I_β. Results from the WRV, Simons' stain and FSP studies indicated that the macro 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.

Effect of damage on fiber bonding

The fiber surface layer studies indicated that the structural elements on the fiber surface layer were separated from each other. The separation of the structural elements might enhance the irregularities on the fiber surface layer, so reducing the bonding area. The bulking of the fiber surface layer, for example, more separated layers, might reduce the ability to resist z-directional stresses. Both the surface irregularities and the separation of the structural elements on the fiber surface might be reasons for the reduced Scott bond values of the mechanically-treated fibers.

Mechanism of fiber wall destruction

Overall 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 fibril (aggregate) skeleton 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. The single fiber strength was not dependent on the degree of fiber deformation but, according to the above hypothesis, on the 3-dimensional arrangement of the structural elements in the fiber wall. This 3-dimensional arrangement in the fiber wall defines the axial load bearing ability of the softwood kraft fiber. The reduced number of contacts between the cellulosic residues of the fiber wall also reduced the load distribution properties of the wall structure during restrained drying, and therefore decreased the fiber segment activation.

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 25.

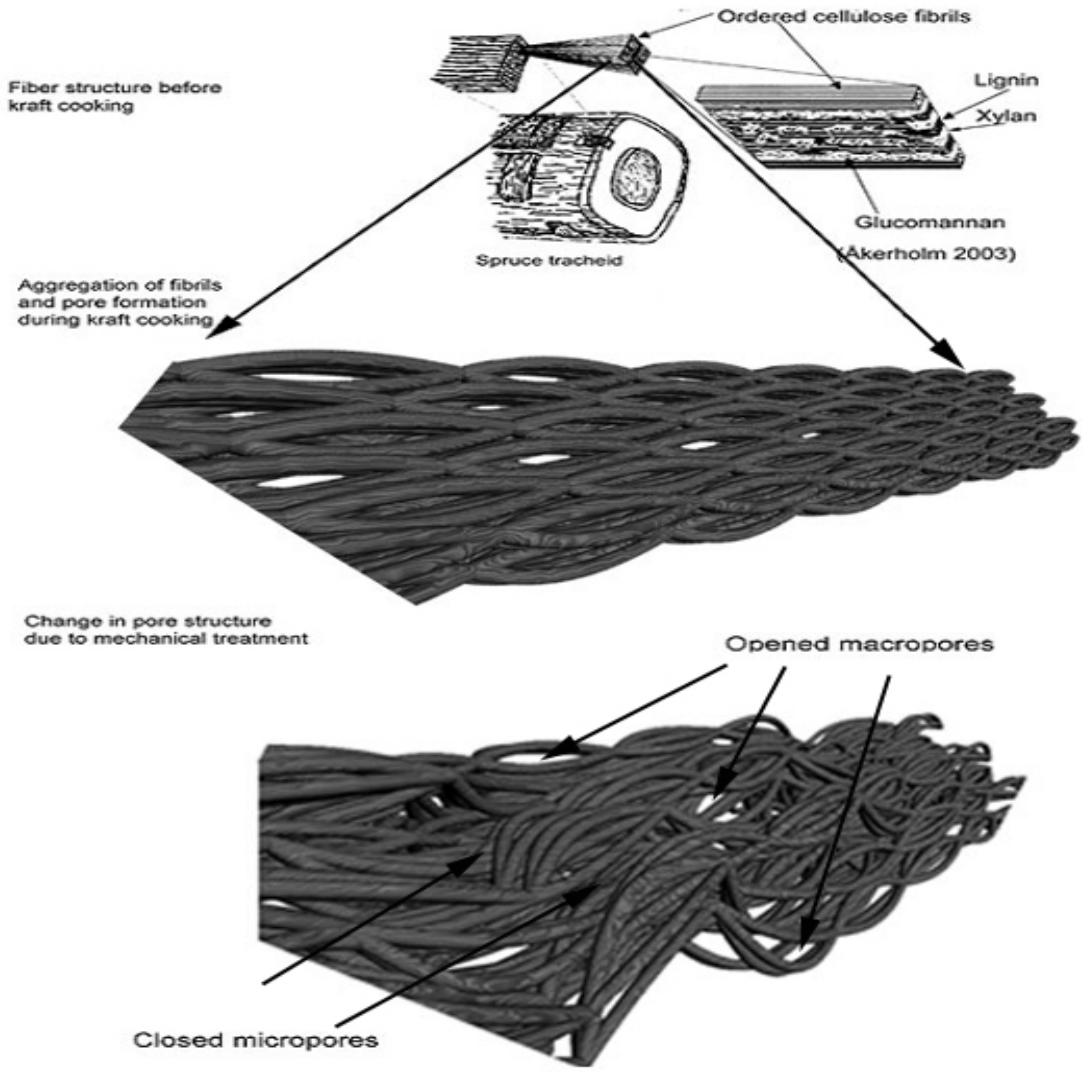

Fig. 25. The proposed mechanism of fiber wall destruction.

During kraft cooking the lignin-hemicellulose matrix between ordered cellulose fibrils is dissolved into 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). 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 25). 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.

This study showed that fiber damage, seen as reduced fiber and fiber network strength, cannot nesessarily be observed on the fiber level. The reasons for the strength reductions are due to changes in the fiber wall macro structure.

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