THE EFFECT OF MECHANICAL TREATMENT ON SOFTWOOD KRAFT PULP FIBERS

Fiber surface layer

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ABSTRACT

Our earlier studies have shown that mechanical treatment of kraft pulp lead to severe strength losses which could not be completely explained by fiber deformations such as curl, kink or dislocations. In this study the effects of mechanical treatment of kraft pulp fibers at high temperature on the surface layers were investigated using several techniques. Neither the fiber surface fibrillation nor fines generation could explain the good z-directional bonding of the mechanically-treated fibers. The contact ratio measurement indicated that the bonding area of the treated pulp was lower, due to the higher curl of the mixed pulp fibers. Atomic Force Microscopy and immunolabelling studies showed that the surface elasticity of the mechanically-treated pulp was more variable and there was more fiber surface accessible. Mechanical treatment also affected the water retention value of the fibers. Differences in water retention value could not be explained by differences in fiber charge. Solid state NMR-studies showed no differences in the polymorphs of the cellulose, which could explain the strength losses.

TIIVISTELMÄ

MEKAANISEN KÄSITTELYN VAIKUTUS HAVUPUUSELLUKUITUIHIN

Kuidun pintakerros

Aiemmat tutkimuksemme ovat osoittaneet, että havupuusellukuitujen mekaaninen käsittely johti rajuun lujuuden menetykseen, jota ei voitu täysin selittää kuitujen deformaatioilla, kuten kiharuus tai kinkkien ja dislokaatioiden määrä. Tutkimuksessa käytettiin useita menetelmiä korkeassa lämpötilassa mekaanisesti käsitellyn kuidun pintakerroksen tutkimiseen. Kuitujen fibrilloitumisella tai suurella hienoaineen määrällä ei voitu selittää mekaanisesti käsitellyn kuidun hyvää z-suuntaista sitoutumista. Kontaktipinta-alamittaukset indikoivat, että mekaanisesti käsitellyn kuidun sitoutumispinta-ala oli pienempi kuin käsittelemättömän kuidun sitoutumispinta-ala, mihin oli ilmeisesti syynä mekaanisesti käsiteltyjen kuitujen suurempi kiharuus. Atomivoimamikroskopia ja vasta-ainemerkintätutkimukset

osoittivat, että mekaanisesti käsitellyn kuidun pinnan elastisuuden vaihtelu oli suurempi ja että sen pinta oli aksessiibelimpi kuin käsittelemättömän kuidun. Mekaaninen käsittely vaikutti kuitujen vedenpidätyskykyyn. Kuitujen varauserot eivät selittäneet kuitujen vedenpidätyskyvyn eroja. Kiinteän tilan NMR-tutkimukset osoittivat, että mekaaninen käsittely ei muuttanut selluloosan polymorfologiaa niin, että sillä voitaisiin selittää lujuuden alenema.

INTRODUCTION

Kraft pulping and subsequent bleaching is one of the most versatile processes for producing pulp for use in paper and board products. The resulting kraft pulp fibers have superior strength properties to fibers produced using other pulping techniques, such as mechanical pulping or sulfite pulping. The significance to the paper maker is that the use of a stronger pulp means that less softwood kraft pulp is required which will result in better optical and surface properties of the paper.

As has been shown in several publications fiber strength is affected by mechanical deformation of the fibers /1, 2, 3, 4/. The relationship between fiber deformation and strength loss along the fiber line, and the increase in fiber deformations in mechanical treatment has been reported by many researchers /5, 6, 7, 8, 9, 10/. The strength studies have concentrated on, for example, different treatments with acid hydrolysis /11/ and enzymatic degradation /12/ with cellulases, which are known to preferentially attack disordered regions in the fiber wall (i.e. in the areas where there already is a local defect). In earlier studies /13, 14/ the authors showed that the strength decrease (tear and tensile strength) caused by mechanical treatment could not be explained totally by cellulose degradation or local defects.

This study concentrates on the nature of the changes on the fiber surface and within the fiber wall after mechanical treatment. Different analytical methods were used to obtain as much information as possible about the changes on and in the fibers.

Experimental

Pulp preparation

The two pulps used in this study were produced from a chip mixture containing 65% pine (Pinus sylvestris) and 35% spruce (Picea abies). About 50% of the raw material was sawmill chips. Two conventional laboratory kraft cooks of the chips were carried out in a digester, which was equipped with a mixing propeller. Cooking conditions were identical with respect to temperature, chemical charge and time. The only difference was that one pulp (designated MIX) was mixed at 350 rpm for 15 minutes before the end of the cook whereas the other (designated NOMIX) was not. DEDED bleaching was performed on both pulps before PFI beating. The sample preparation is presented in Table 1. The pulping procedure is presented in more detail in reference 14.

Table 1. The sample preparation of the pulps used in the study. Typical bleaching conditions to achieve a brightness of 88%.

Sample			Digester		Mixing	
NOMIX			Digester with mixing propeller		30 rpm stirring during cooking	
MIX170			Digester with mixing propeller		30 rpm stirring during cooking and mixing at 350 rpm at 170°C started 15 minutes before end of cook	
Bleaching conditions						
Stage	Charge, % ClO_2	NaOH	Temperature, °C	Consistency, %	Time, min	Washing
Do	6.36	-	50	3	60	Ion-exchanged water: 2x10x amount of pulp, between stages.
E1	-	2.86	60	10	60	
D1	2.52	-	70	10	150	
E2	-	0.80	70	10	60	
D2	1.1	-	70	10	150	

Hand sheet preparation and 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 viscosities 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.

Analytical methods

Fiber width

The widths of unbleached pulp fibers were measured using a light microscope and semi-automatic image analysis using a wet (water/glycerol) longitudinal fiber preparation. The average fiber width was measured so that the mean site of the fiber was pointed and measured automatically under transmitted light illumination. The widths of 200 fibers were measured.

Fines content

The fines contents of bleached MIX and NOMIX pulps were measured with a Dynamic Drainage Jar (DDJ) and a Kajaani FS-200 after 0, 1000 and 2000 PFI revolutions. The DDJ measurement was carried out according to SCAN CM-66:03 6th proposal and according to reference 15.

External fibrillation

External fibrillation was studied using light microscopy and fibers that had been stained with Congo Red. The magnification was 100x, and 600 fibers were examined per analysis. The fibers were divided into three classes: intact or slightly fibrillated; fibrillated without serious fiber wall damage; and broken or showing damage at several points in the fiber wall.

Contact ratio

The bonding potential or contact ratio (CR) technique is based on an observation made by Clarke /16/. The method /17, 18/ involves drying a thin fiber suspension in contact with a clean glass slide. The sample is inverted and examined under transmitted illumination. This view gives a measurement of the total projected fiber area. The same field is then examined under incident illumination and a measure of the area that is in optical contact with the glass slide is made. The ratio of optical contact area to total fiber area is known as the contact ratio.

The analysis was carried out using wet unbleached MIX and NOMIX pulps (dry matter content approximately 28%). Pulp was pressed to a piece of glass (1x50x75mm) using a British sheet mould, to 0.1g/m^2. The pressure was 4 kp/cm^2 and the pressing time was 2 minutes. The pressed glass with fibers was dried at room temperature for one hour. Before pressing the fibers onto the glass, it was first cleaned in an ultrasonic bath containing chrome sulfuric acid. The glass was rinsed with cold and hot ion- exchanged water (and then with methanol). The rinsed glass was dried at 105^{o}C for 1 hour.

The measurements were done with a light microscope of 100 fields (field area of 852µm x 852µm). Fibers crossing each other were neglected from the measurements. The images under transmitted and incident illumination were analyzed with a Zais KS-400 Image Analysis program. Two identical runs were performed and the image area ratios were calculated.

Fiber surface elasticity

An Atomic Force Microscope (AFM) was used to investigate possible surface changes. The AFM probed the surface of a sample with a sharp tip (less than 10 nm in diameter). Forces between the tip and the sample surface cause a cantilever tip to bend, or deflect as the tip is scanned over the sample. The measured cantilever deflections allow a computer to generate a surface topography. In addition the phase imaging AFM produces images that show local variations in sample stiffness, adhesion and chemical interactions /19/. The device used in this study was a NanoScope IIIa (Digital Instuments). The samples were wet unbleached MIX and NOMIX pulps. The measurements were carried out in an air atmosphere at 23 ^{o}C and relative humidity of 30%. The measurements were done in tapping mode and the phase detection mode pictures were saved at the same time. The free oscillation of the tip was 280-300 kHz and the amplitude was 2V (equal to 25nm). The set point amplitude was 1.3V. The phase detection mode signal was adjusted to zero always before taking a new measurement. Seven different areas were measured for both samples. The sample stiffness

was analyzed from measured data and the gray-value distributions of the pictures were calculated. The measurements were carried out at Helsinki University of Technology (Finland).

Labelling of the fiber surface layer

Immunolabelling of the unbleached pulps was used to study the surface structure of fibers using a specific antibody. Polyclonal antibodies specific to xylan and lignin were produced in rabbits using methylglucuronicacidxylan$_{2\text{-}3}$ (MeGlcAXyl$_{2\text{-}3}$) and spruce lignin as antigens, respectively. The antibodies became attached to the antigens on the fibers. Commercial anti-rabbit antibody coupled to a Cyan-5 (Cy-5) fluorescent label (Sigma) was used as a secondary antibody. Immunolabelling was performed as described in reference /20/. Microscopic examination was performed using Confocal Laser Scanning Microscopy (CLSM, Bio-Rad) using excitation wavelengths of 638nm and 488nm for Cy-5. The antibody labeling and the production of pictures were carried out at VTT Biotechnology (Finland). Image analysis of the pictures was carried out using a Soft Imagining Systems image analysis program. The images of the immunolabelled fibers were color separated according to the color used in the immunolabelling. The gray values of color-separated images were measured as an indication of immunolabelling intensity.

Fiber charge

The accessibility of the charges in the fibers was evaluated by adsorption of poly (dimethyldiallylammonium) chloride, "poly-DMDAAC". The poly-DMDAAC has a distribution of three different molar masses ($3\bullet10^4< M_w<5\bullet10^4$, $1\bullet10^5<M_w<3\bullet10^5$ and $M_w>3\bullet10^5$) and a charge density of 6.19 $\bullet10^{-3}$ eq/g). Determinations of polyelectrolyte adsorption and pulp pretreatments were done using the method described by Wågberg et.al. /21/. The titration was performed in two ways: directly from the fiber suspension (which gives the charge density of the suspension) and then after fiber removal from the suspension.

Cellulose morphology

The different polymorphs of cellulose was studied in the unbleached MIX and NOMIX pulps using ^{13}C CPMAS NMR (Carbon-13 Cross-Polarization Magic Angle Spinning Nuclear Magnetic Resonance) spectroscopy /22/. The measurements were performed at the University of Helsinki (Finland).

Results and discussion

The effects of mechanical treatment during cooking on fiber and strength properties of pulps, especially the effect on fiber bonding, were studied. Changes within the fiber surface layer and changes in fiber charge and morphology resulting from mechanical treatment were evaluated using different analytical methods and the results are discussed below.

Pulp properties

Table 2 shows that the pulp that had been mixed had a slightly lower kappa number than the one that had not been mixed. A more even temperature distribution as a result of mixing at the end of the cook might explain this. The cooking yield and viscosity of the mixed pulp at a temperature of 170°C were lower than for the NOMIX pulp. However, when yield and viscosities were calculated to the same kappa number level (interpolated and extrapolated to kappa level 30 so that it was assumed that one kappa unit was equal to 0.17 units of yield and 16 units of viscosity) there were no differences between the pulps. The fiber length of the bleached MIX pulp was the same as that of the NOMIX pulp, in spite of mixing. This indicated that the fibers were not cut during mixing. The WRV of the unbleached MIX pulp was lower than that of the unbleached NOMIX pulp.

Table 2. Pulp properties of unbleached and bleached mechanically-treated MIX pulps (at a temperature of 170°C) and NOMIX pulp.

Pulp	Analysis	MIX	NOMIX
Unbleached	Kappa	27.0	33.4
Unbleached	Viscosity, ml/g	1250	1360
Unbleached	Yield, %	47.9	48.9
Unbleached	WRV, g/g (unbeaten)	1.5	1.8
Bleached	L.w.av.* fiber length	2.26	2.33
Bleached	Coarseness, mg/m	0.246	0.229
Bleached	Viscosity, ml/g	1090	1210

*Length weighted average

Strength properties

The pulps were bleached using a DEDED sequence to a brightness of 88% and beaten in a PFI beater. The number of PFI revolutions required to achieve tensile indices of 50 N•m/g and 70N•m/g are shown in Table 3. Table 3 also shows the tear index, Scott Bond, zero-span index (measured from rewetted sheets) and light scattering for MIX and NOMIX pulps.

Table 3. PFI revolutions, tear index, bulk, Scott Bond and zero-span tensile index at tensile indices of 50 N•m/g (T50) and 70•Nm/g (T70) measured for unbleached and bleached MIX and NOMIX pulps.

	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 @ PFI 0 revs.	23.1	51.7	21.1	30.3
Zero-span (wet), N•m/g @PFI 0 revs.	102.9	147.2	100.1	124.4
Tear ind, mN•m2/g @T50	13.9	24.3	17.8	26
Tear ind, mN•m2/g @T70	9.5	18.8	11.7	19.7
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
Bulk, dm^3/kg @T50	1.63	1.69	1.48	-
Bulk, dm^3/kg @T70	1.49	1.49	1.44	1.46
Zero-span (wet), N•m/g @T50	114.1	147.2	119.7	132.5
Zero-span (wet), N•m/g @T70	139.5	150	123.8	142.6

There were significant differences between the beating responses of the unbleached and bleached MIX and NOMIX pulps (Table 3). The MIX pulp required twice as many PFI revolutions to reach the same tensile index as the NOMIX pulp. The zero-span tensile index and tensile index values of the MIX pulp at 0 PFI revolutions were both very low compared to those of the NOMIX pulp. It has been reported that fiber curliness /23, 24, 25/, hemicellulose content /26/ and the swelling /27/ affect the development of the tensile and zero-span tensile indices during beating. To eliminate the effect of fiber curl on these measurements, the latter should be performed on straight fibers /23, 25/. Because of this, it was expected that the zero-span and tensile index values would be lower for the MIX pulp at the beginning of beating, and this was the case. However, in our earlier study /13/ the MIX pulp had lower curl values than the NOMIX pulp at the end of beating, yet the zero-span tensile and tensile index values were still lower.

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. However, at the same number of PFI revolutions the Scott bond values were slightly lower for the MIX pulp than for the NOMIX pulp (Table 3). This was probably related to the parameters that influence bonding: fines content /28/, fiber dimensions, fiber strength and relative bonded area, which is dependent on the swelling of the wet fibers /26/. Usually WRV is considered to be a measurement of fiber swelling and thus it seems appropriate to relate WRV to properties influenced by fiber flexibility /26/ (i.e. tensile index and Scott bond). However, the WRV and the tensile index measured for unbleached and unbeaten NOMIX and MIX pulps showed that the fiber swelling and tensile indices were not at the same level but the Scott Bond values were (Tables 2 and 3).

The fines content is reported to enhance bonding in the pulp sheet structure /28/. The fines were measured in bleached MIX and NOMIX pulps using a DDJ (unbeaten), and from beating points 0, 1000 and 2000 revolutions using the Kajaani FS-200. The results are shown in Table 4.

Table 4. The fines content measured from bleached MIX and NOMIX pulps.

DDJ FINES,% (UNBEATEN)		KAJAANI FS-200, FINES, %, PFI REVS.	MIX	NOMIX
MIX	NOMIX			
2.3	2.5	0	2.56	2.75
		1000	2.49	2.34
		2000	2.47	2.45

Table 4 shows that neither fines content measurement showed any significant difference between the pulps. Of course, it is possible that the fines material generated from the MIX pulp caused a greater enhancement of bonding compared to that in the NOMIX pulp, but the nature of the fines was not studied here.

Fiber widths measured for the unbleached MIX and NOMIX pulps are shown in Table 5.

Table 5. Fiber width measured for unbleached MIX and NOMIX pulps.

SAMPLE	AVERAGE WIDTH	STANDARD DEVIATION
NOMIX	35.08 μm	10.27
MIX	41.22 μm	12.92

The average fiber width of the MIX pulp was slightly higher than that of the NOMIX pulp. The difference between the pulps, however, was negligible and fell within the standard deviation.

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 6.

Table 6. The degree of fibrillation of the bleached MIX pulp after 0 and 2000 PFI revs. and the bleached NOMIX pulp after 0 and 1000 PFI revs. (2000 PFI revs and 1000 PFI revs give approximately equal tensile indices for MIX and NOMIX pulps respectively).

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 6), which meant that the mechanical treatment did not fibrillate the outer fiber surface. Table 6 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 pulp were subsequently studied more closely in order to find explanations for the different behavior of the fibers.

Fiber surface

The contact ratios of the unbleached, unbeaten MIX and NOMIX fiber surfaces were measured in order to obtain information on how the mechanical treatment at the end of cooking had affected the bonding ability of the fibers. The results from these measurements are presented in Table 7.

Table 7. Contact ratios of the unbleached, unbeaten MIX and NOMIX pulps.

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	20.3

Table 7 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. These values, however, were the same for the MIX and NOMIX pulps (Table 3). 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.

According to the literature/29, 17/ there should also be a correlation between contact ratio and tensile index. 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 different correlations between contact ratio and Scott Bond and contact ratio and tensile index could be that in the contact ratio measurement, the pulps dried differently on the glass surface. For example, deformed fibers (MIX pulp) shrank in 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, form a less uniform surface layer than the NOMIX pulp fibers. This kind of bulking of the outer fiber surface could have enhanced bonding of the fibers in a fiber network. This hypothesis was studied with Atomic Force Microscopy (AFM) and immunolabelling of the fibers.

AFM was used to study the surface differences between the fibers of the MIX and NOMIX pulps. The fibers were imaged in tapping mode, capturing dual height and phase images. The gray-value distributions of the phase images are shown in Table 8 (presented as mean value and standard deviation).

Table 8. Gray value distributions, presented as mean value and standard deviation, (the standard deviation describes the distribution) measured from the AFM phase pictures of the unbleached MIX and NOMIX pulp fiber surfaces.

Sample	Tip angle, degree	Average gray value	Standard deviation Gray value
NOMIX	40	13.0	9.7
	40	12.8	9.0
	40	14.2	11.0
	35	13.8	10.4
	50	18.4	15.0
	50	18.5	14.1
MIX	18	6.2	4.5
	18	6.2	4.6
	35	11.8	8.2
	40	12.6	7.7
	60	21.6	17.3
	60	23.6	19.4

Despite the small number of AFM pictures (only six for each fiber type), it may be concluded that mixing broadens the gray value distributions, (mean values: NOMIX 13-18.5 vs. MIX 6.2-23.6). This indicated that the fiber surfaces of the MIX pulp consisted of more elastic and less elastic structures compared to the fiber surfaces of the NOMIX pulp. The problem with AFM is that the area of interest is so small that it can lead to incorrect conclusions.

The immunolabelling method was used to study the surface structure of the fibers of the MIX and NOMIX pulps. The results of the studies are presented in Table 9.

Table 9. Mean gray-value ROI (Region Of Interest) calculated from CLSM pictures taken from labelled unbleached MIX and NOMIX pulps (the intensity of antibody on that fiber surface).

Sample	*Area Fraction, %*	*Grayvalue Mean ROI*	*Grayvalue StdDev ROI*
NOMIX	54.5	89.0	58.9
MIX	58.0	97.5	56.8

The results in Table 9 indicate that the area of labeling of the MIX pulp fibers was slightly larger, and the labeling more intense than for the fibers of the NOMIX pulp. This meant that there was more antibody associated with the surface areas of the mixed fibers than the unmixed fibers. This indicated that the surface of a mixed fiber was more accessible to labeling. 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 specific to xylan or lignin. In spite of the small number of pictures the calculations indicated that the area

fraction and intensity of the region of interest of the mixed fibers was greater.

Fiber Charge

It has generally been observed that 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 /30/. Because the swelling decreased as a result of mixing, fiber charge was measured for the unbleached and unbeaten MIX and NOMIX pulps. Table 10 shows the results of the fiber charge measurements.

Table 10. The fiber charge of unbleached and unbeaten NOMIX and MIX pulps.

Sample	*Charge(titrated from fiber suspension),µeq/g fiber*	*Charge (titrated from liquid after fiber removal)µeq/g fiber*
NOMIX	-25.3	-30.4
MIX	-25.9	-36.7

Table 10 shows that there were no differences in the charge results obtained for the MIX and NOMIX pulps. According to Laine /31/ the WRV values and fiber flexibility increased as the charge of the bleached soft wood fibers increased. Emerton /32/ and Scallan /33/ have also shown that the plasticisation of the cell wall (i.e. the penetration of water) causes debonding and separation of solid elements (microfibrills, lamellaes) and increases with the degree of swelling. This plasticisation loosens the cell wall structure and affects the flexibility of fibers. One possible explanation for the high Scott bond values of the MIX pulp fibers could be that the mechanical treatment had enhanced the plasticisation (i.e flexibility) of the cell walls of the MIX fibers, thereby enhancing bonding.

Cellulose morphology

It has been suggested, that the differencies in cellulose polymorphs of cellulose micro fibrils would influence the strength properties of wood fibers /34/. According to Liitiä /22/, in pulping part of the cellulose I_α is converted to the more stable form I_β, and this is mainly induced by heat. The MIX and NOMIX fibers were studied using solid state NMR to determine whether the mechanical treatment during pulping had induced morphological differences between the pulps. The study was carried out using unbleached and unbeaten fibers. The results are shown in Table 11.

Table 11. The results of solid state NMR study obtained for unbleached and unbeaten MIX and NOMIX fibers.

Sample	*Degree of Crystallinity, %*	*Cellulose I_α, %*	*Cellulose I_β, %*
Unmixed	52	27	73
Mixed	53	25	75

Table 11 shows that the mechanical treatment did not changed 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. The reasons for the strength loss must be related to differences in the fiber wall other than cellulose morphology.

Conclusions

The pulp properties of damaged and undamaged pulps were measured and the effect of mechanical treatment on the strength properties of pulps, especially on fiber bonding, was analyzed. Changes to the fiber surface layer, charge and morphology resulting from mechanical treatment were evaluated using different analytical methods. The results showed that:

- The MIX pulps fibers were much weaker than the NOMIX fibers.
- The binding surface of the MIX pulp fibers was smaller than that of the NOMIX fibers. This was obviously due to the higher fiber curl of the MIX pulp fibers, which also lead to a lower tensile index.
- There was more variation in the surface elasticity of the MIX pulp fibers than of the NOMIX fibers, which might have enhanced the z-directional fiber bonding (Scott Bond).
- The antibody studies indicated that the surface properties of the mixed fibers were affected and this was seen as differences in labelling intensity. This indicated that the fiber surface would have been more accessible than that of the NOMIX pulp fibers.
- The higher unbeaten Scott bond values of the MIX pulp compared to those of the NOMIX could not be explained by the higher fines generation of the MIX pulp fibers resulting from mechanical treatment or by the higher degree of fibrillation of the fiber surface.
- The mechanical treatment of kraft pulp fibers reduced the WRV of the unbeaten and unbleached fibers.
- The lower water holding ability (WRV) of the MIX fibers could not be explained by changes in the fiber charge.
- The polymorphology was studied with solid state NMR, but no changes were detected, which could explain the strength losses.

It seems that the severe strength loss due to mechanical treatment of kraft pulp at high temperature and alkali concentration could not be explained totally by fiber deformations or changes to the fiber surface or cellulose morphology.

References

1. Hägglund, E., Om fiberstrukturens förändring vid vissa slag av sulfit- och sulfatkokningar Svensk Papperstidn. 38(1935): 5, 145-154.

2. Knutson, T., Stockman, L., The Effect of Treatment During the Final Stages of the Cook on the Beating Properties and Strength of Sulphate pulp. Tappi J. 41(1958):11, 704-709.

3. Annergren, G.E., Öhrn, O. E., Rydholm, S. A., Kraft pulp quality from batch and continuous cooking. Svensk Papperstidn. 66(1963):4, 110-114.

4. Bennington, C. P. J., Seth, R. S., Response of fibers on mechanical treatment during MC fluidization. Fundamentals of papermaking. Transactions of the 9th Fundamental Research Symposium held Cambridge. 17-22 September 1989, ed. by C.F. Baker and V. W. Punton. Vol. 1. Mechanical Engineering Publications Limited, London. pp. 87-104.

5. MacLeod, J.M., Cyr, M., Embley, D., Savage, P., Where the strength is lost in kraft pulping of softwoods. J. Pulp Paper Sci. 13(1987):5, J87-J92.

6. MacLeod, J.M., Pulp strength along the complete kraft pulp mill fiber lines. Tappi J. 78(1995):8, 153-160.

7. Page, D.H., Seth, R. S., The elastic modulus of paper III. The effect of dislocations, microcompressions, curl and kinks. Tappi 63(1980) 10, 99-102.

8. Seth, R.S., Zero-span tensile strength of paper making fibers. Pap. Puu 77 (2001):8, 597-604.

9. Clark, T.A., Ellis, M.J., Softwood kraft pulp strength – its measurement and the effect of fiber deformations. 51st Appita Annual General Conference, Melbourne, Australia, Apr. 28-May 2, 1997, Vol. 2, pp. 573-580.

10. Pihlava, M., Fiber deformations and strength loss in kraft pulping of softwood, Licenciate Thesis, Helsinki University of Technology, 72 p., 1998.

11. Berggren, R., Berthold, F., Sjoholm, E., Lindstrom, M., Fiber strength in relation to molecular mass distribution of hardwood kraft pulp.Degradation by ozone and acid hydrolysis. Nord. Pulp Pap. Res. J. 16(2001)4, pp 333-338.

12. Gurnagul, N., Page, D. H., Paice, M.G., The effect of cellulose degradation on the strength of pulp wood fibers. Nordic Pulp Pap. Res. J. 7(1992):3, 152-154.

13. Joutsimo, O., Robertsén L., Fiber Damage due to mixing. The 4th Biennial Johan Gullichsen Colloqium 2003, 10 September 2003, Espoo, Finland, pp. 25-31.

14. Joutsimo, O., Robersen, 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.

15. Pelton, R., Allen, L.H., Nugent, H., Newsprint pulp fines retention measurements with dynamic drainage jar. CPPA Technical Section 65th Annual meeting, Montreal, Canada, Feb. 1-2, 1979, pp. B111-B117.

16. Clarke, B., Furnish blend optimization and evaluation. Paper Maker, 41 (1972):4, 38-39, 41.

17. Howard, R.C., Kropholler, H.K., Bonding measurement by image analysis. Pulp Pap. Mag. Can., 81(1980)12, T334-T338.

18. Sloane, C. M., A preliminary study of the effect of recycling on the bonding potential of unbleached radiata pine and Scandinavian spruce kraft pulps. Appita Annual General Conference, Melbourne, Australia, Apr. 19-23, 1993, Vol. 2, pp. 533-540.

19. Österberg, M., On the Interactions in Cellulose Systems: Surface Forces and Adsorption. Doctoral thesis, KTH, Stockholm 2000, 63 p.

20. Pere, J., Lappalainen, A., Tenkanen, M., Immunochemical methods for chemical mapping of fibres, Microscopy as a Tool in Pulp and Paper Research and Development, Stockholm, Sweden, 21-22 June1999, p. 90.

21. Wågberg, L., Winter, L., Lindström, T., Determination of ion-exchanged capacity of carboxymethylated cellulose fibers using colloid and conductometric titrations. Papermaking Raw Materials: Their interaction with the production processes and their effect on paper properties. Fundamental Research Symposium, Oxford, September 1985, ed. by V. Punton. Vol. 2, Mechanical Engineering Publ. Ltd. London, pp. 917-923.

22. Liitiä, T., Maunu, S-L., Hortling, B., Solid State NMR Studies on Cellulose Crystallinity in Fines and Bulk Fibres Separated from Refined Kraft Pulp. Holzforschung. 54(2000)6, 618-624.

23. Seth, R.S., Zero-span tensile strength of papermaking fibres, Pulp and Paper Research Institute of Canada, 85th Annual meeting, Montreal, Canada, 26-29 Jan. 1999, Preprints A, pp. A161-A173.

24. Omholt, I., The effects of curl and microcompresisons on the combination of sheet properties, Norwegian Pulp and Paper Research Institute, 1999 International Paper Physics Conference, San Diego, CA, USA, 26-30 Sept. 1999, pp. 499-515.

25. Page, D.H., Seth, R.S., Jordan, B.D., Barbe, M.C., Curl, crimps, kinks and microcompressions in pulp fibers- their origin, measurements and significance. Paper making raw materials: their interaction with the production process and their effect on paper properties. Transactions of the 8th Fundamental Research Symposium, Oxford, September 1985, ed by V. Punton. Vol. 1, Mechanical Engineering Publ. Ltd. London, pp. 183-227.

26. Paavilainen L., Influence of fiber morphology and processing on the softwood sulphate pulp fiber and paper properties, Dissertation at Helsinki University of Technology, 1993, 155 p.

27. Stone. J. E., Scallan, A. M., A structural model for the cell wall of water-swollen pulp fibers based on their accessibility to macromolecules. Cellulose Chem. Technol. 2(1968), 343-358.

28. Panula-Ontto. S., Fractionation of unbleached softwood kraft pulp with wedge wire pressure screen and hydrocyclone, Licenciate Thesis, Helsinki University of Technology, 2003, 86 p.

29. Hamer, R.J., The characterization of stock properties. Paper Technology, 15(1974)5, T153-T160.

30. Lindström, T., Chemical factors affecting the behaviour of fibers during paper making. Nord. Pulp Pap. Res. J. 7(1992): 4, 181-192.

31. Laine, J., The effect of cooking and bleaching on the surface chemistry and charge properties of kraft pulp fibers. Dissertation at Helsinki University of Technology, 1996, 55p.

32. Emerton, H.W., Fundamentals of the beating process, British Paper and Board Industry Research Association, Kenley 1957, 198 p.

33. Scallan, A.M., The effect of acidic groups on the swelling of pulps: A review. Tappi J. 66(1983):11, 73-75.

34. Ishikawa, A., Okano, T., Fine structure and tensile properties of ramie fibers in the crystalline form of cellulose I, II, III_1 and IV_1. Jpn. Wood Res. Soc. 43(1997)4, 337-341.