

IMPROVEMENT OF PAPER STRENGTH BY INCREASING THE XYLAN CONTENT

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ABSTRACT

Extracted xylan from beech dissolving pulp and eucalyptus kraft pulp was precipitated on unrefined, bleached, once-dried softwood kraft pulp and sulfite pulp. The temperature, pH, ionic strength, xylan concentration, pulp consistency, and the dwell time were analyzed regarding their influence on the adsorption of xylan. Furthermore, handsheets were made to investigate the impact of xylan on the tensile strength and the tearing resistance of the paper. The swelling behavior of the fibers was of interest as well as the determination of the total and surface charge of the pulp.

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The xylan content of the fibers could be significantly increased. The temperature, xylan concentration and ionic strength showed a large influence on precipitation. No significant change in the attachment of xylan between neutral and low alkaline level of the pH could be noticed. A higher pulp consistency, including a sufficient mixing during adsorption, is favorable. Xylan shows a large impact on the tensile strength of the softwood handsheets. The tensile index of the handsheets made of the softwood pulp and refined at 3.000 revolutions with a PFI mill could be increased by up to 38% compared to the reference sample. The xylan-modified samples also showed by trend a higher stretch at break of about 0.5%. This could be the result of a higher surface area and total charge of the fibers. Thus, enhanced swelling is caused leading to softer and more flexible fibers. These effects provoke a larger area in molecular contact. On the other hand, the trend of the tear index of the softwood handsheets with an increased amount of xylan declines stronger after a longer time period of refining.

Keywords: Xylan, adsorption, HPLC, ^1H NMR spectroscopy, strength properties, fiber charge.

1 INTRODUCTION

Xylan is one of the most common native biopolymers in higher plants and wood, e.g. hardwoods contain up to 35% of xylan [1]. In xylan the xylose units are covalently linked by β -(1,4)-glycosidic bonds to a homopolymer backbone. Compared to cellulose, wood xylans are branched with various side groups. 4-O-methyl- α -D-glucurono-D-xylan (MGX) is the main hemicellulose component in hardwoods, on which 4-O-methylglucuronic acid residues (MeGlcA) are irregularly attached to the backbone by α -(1,2)-glycosidic bonds. Furthermore, native hardwood xylans contain O-acetyl groups and can also exhibit small amounts of rhamnose and galacturonic acid. In contrast, softwoods have a considerable quantity of (arabino)glucuronoxylan (AGX). The backbone is branched by α -L-arabinofuranose residues, which might also have a slight amount of O-acetyl groups. In addition, AGX is more heavily substituted by MeGlcA than the MGX [1–4].

Chemical pulping leads to an increased dissolution rate of xylans with increasing temperature during the early stage of the cook [5–7]. Further, hydrolysis and peeling reactions take place, changing the chemical structure of xylan in the cooking liquor and can also reduce the molecular weight. Moreover, the concen-

tration of cooking chemical, e.g. NaOH in the kraft process, is decreasing at the end of cook, which will lead to a reduction of dissolved xylan as well [1, 8–16]. The elimination of MeGlcA from the backbone results in a lower solubility and promotes deposition of dissolved xylan onto cellulose to a certain amount [17–20]. However, the dissolution of xylan is higher than the redeposition and causes a reduction in paper strength [21–24].

A large number of experimental studies have been performed in the past, e.g. [25–33], to enhance the yield after cooking by adsorption of the dissolved xylan and to understand the mechanism(s) and the driving variables, e.g. temperature, pH, ionic strength, xylan concentration, or dwell time, during redeposition. The improvement of the strength properties of the paper was also of interest. Nevertheless, the mechanism of the deposition of xylan is not clearly understood. Henriksson and Gatenholm [30] assumed, that the adsorption of xylan onto cellulose is not just a crystallization, but also a process of changes in the solubility and/or colloidal stability of xylan as well as the affinity between xylan and cellulose. Linder et al. [34] proposed, that colloidal dissolved molecules and aggregates of xylan can diffuse to and then adsorb onto cellulose surfaces. Moreover, they noticed a growth of xylan aggregates, due to the autoclave treatment by either chemical changes of the structure of xylan—lowering the solubility—or by physical factors.

This work studies the deposition of different xylans on the surface of bleached, once-dried softwood kraft and sulfite fibers to improve their mechanical strength properties. The main aim is to analyze the driving forces for the adsorption of xylan onto cellulose to identify conditions resulting in the highest xylan adsorption. The influence of the zeta potential of the different xylans and the fibers during adsorption is of interest. Further, the total charge and surface charge of the modified and unmodified pulp samples were determined. Efficient retention with respect to possible sites of xylan addition in the mill is also taken into account.

2 EXPERIMENTAL

Adsorption experiments have been performed to analyze the influence of six variables on the adsorption behavior of xylan onto cellulose fibers. Two different pulps were used, unrefined, once-dried, bleached soft wood kraft pulp (a mixture of pine and spruce) and a sulfite pulp (a mixture of soft and hardwood). The pulp samples were evaluated regarding their chemical composition, mechanical strength properties, and suspension properties. The experiments and analysis were done with the softwood kraft pulp. The sulfite pulp was used to investigate first findings on another type of pulp with different surface and mechanical characteristics.

2.1 Pulp preparation

Dry softwood kraft pulp (bale form) was soaked in deionized water for at least 4 h and disintegrated for 25 min (*ISO 5263-2:2004*). After the removal of fines, using a 100 μm mesh, the pulp was thickened to a dry content of about 20% and stored in a refrigerator until use.

The same procedure was done with the sulfite pulp (sheet form). Only the time for the disintegration was reduced to 10 min (*ISO 5263-1:2004*).

2.2 Xylan preparation

For the investigations two different xylans (powder form) were used. Xylan 1 (X1) was extracted from a beech sulfite dissolving pulp and xylan 2 (X2) from eucalyptus kraft pulp.

The chemical composition of both xylans—depolymerized by acid methanolysis—was determined by gas chromatography, as can be seen in Table 1. The xylose content was about 90% for both xylans, whereas X1 had a higher content of uronic acid residues (MeGlcA) of about 4.8%, compared to 3.7% for X2. Further, X1 had a small amount of mannose (0.4%) and X2 consisted 0.4% galactose. In both xylans, a small amount of glucose (X1 (0.8%) and X2 (0.2%)) was present. During the alkaline xylan extraction process most likely degraded and therefore short-chained cellulose is dissolved. In the following washing steps, where the pH is significant lowered, these cellulose molecules are again able to precipitate and deposit with the xylan. This might be the reason for the small amount of glucose in the extracted xylans, determined via acid methanolysis and gas chromatography.

Differences could be found in the molecular weight of both xylans. The molecular weight (weight average) of X2 (17.9 kDa) was almost twice as high as that of X1 (9.0 kDa), as can be seen in Table 2.

Table 1. Chemical composition of the used xylans, depolymerized by acid methanolysis and determined via gas chromatography

	<i>X1</i>	<i>X2</i>
<i>Monomer</i>	%	%
MeGlcA	4.8	3.7
Arabinose	0.1	0.0
Galactose	0.0	0.4
Glucose	0.8	0.2
Mannose	0.4	0.0
Rhamnose	0.0	0.0
Xylose	90.6	89.4
total	96.7	93.9

Table 2. Molecular weight of the used xylans, determined by size-exclusion chromatography.

<i>Molecular weight</i>	<i>X1</i>	<i>X2</i>
	<i>kg mol⁻¹</i>	<i>kg mol⁻¹</i>
number average	4.6	5.6
weight average	9.0	17.6

The xylans were added to NaOH (1 mol L⁻¹) and stirred for 15 min (X1) and 25 min (X2), respectively, and heated to about 55°C to ensure a complete dissolution. However, in case of X2, undissolved parts were still remaining, resulting in a turbid solution. Before usage, the solution was cooled to room temperature.

2.3 Influencing variables on adsorption

The variables temperature (T), duration time of adsorption (t), pH, ionic strength (IS), xylan concentration (XC) in the pulp suspension, and the pulp consistency (C) were adjusted to different values to investigate their influence on the assembly of xylan on the pulp fibers. The set values of the variables can be seen in Table 3.

2.4 Adsorption experiments

The adsorption experiments at 40°C and 80°C were performed with Erlenmeyer flasks, which could be sealed with a stopple and a bail. The trials at 140°C were carried out using lab-scale steel autoclaves.

First, the pulp was put into a flask. A certain amount of NaCl was dissolved in deionized water to set the IS to the given value. The water was added to the pulp

Table 3. Values of the investigated variables during adsorption.

<i>Variable</i>	<i>Unit</i>	<i>Values</i>
C	%	1.0; 2.5; 5.0; 10
IS	mol L ⁻¹	0.25; 1; 2
pH		7; 10; 12.6
t	h	0.5; 1; 2; 3
T	°C	40; 80; 140
XC	%	4; 8; 16; 32

and the suspension was mixed, in order to separate the fibers. Then, the xylan solution was added to the suspension and the final pulp consistency was reached. Before the dosage of xylan, the pH of the solution was adjusted with H_2SO_4 . The flask was sealed, heated to the desired temperature and placed in a heated water bath. In case of the trials at 140°C , the same procedure was performed in autoclaves. For heating up, the autoclaves were sealed and a heater band was placed around. After the desired adsorption time, the pulp was washed with deionized water until the conductivity was below $10\ \mu\text{S cm}^{-1}$.

2.5 Chemical analysis of the pulp

The chemical composition of the pulp samples, before and after adsorption, were analyzed by high-pressure liquid chromatography (HPLC) and ^1H nuclear magnetic resonance (NMR) spectroscopy.

2.5.1 High-pressure liquid chromatography

Before the analysis, the pulp samples were milled, dissolved and degraded to their sugar monomers in a two-stage hydrolysis by H_2SO_4 , according to Sixta et al. [35].

A known pulp mass equivalent to approximately 40 mg was placed in a 10 mL centrifuge tube and 0.5 mL of 72.3% H_2SO_4 was added. The slurry was stirred for 3.5 h at around 25°C . Then, 8.5 mL of deionized water was added, the tubes were sealed and placed in a heatable rotator at $110^\circ\text{C} \pm 1.0^\circ\text{C}$ for 90 min. The tubes were removed and chilled in a water bath to room temperature.

Before the HPLC analysis, a certain amount of the hydrolyzed sample was diluted with 0.1% w/w of NaOH to a ratio of 1:50 w/v. This was done to set the pH in the neutral range in order to avoid deposits in the separation column. A further part of the hydrolyzed sample was diluted with deionized water to analyze the content of furfural, which is formed during the dissolution and degradation of xylan. Afterwards, the samples were transferred to a cuvette and analyzed. For the separation of the sugar monomers a Dionex CarboPac™ PA10 ($4 \times 250\ \text{mm}$) was used. The detection of the monomers was accomplished with pulsed amperometric detection (Dionex ED40).

2.5.2 Nuclear magnetic resonance spectroscopy

The milled pulp samples were hydrolyzed in a two-stage hydrolysis by H_2SO_4 to their sugar monomers. The acid hydrolysis was performed as described by Bose et al. [36]. They tested different hydrolysis conditions on two softwoods and analyzed the hydrolyzed samples, until the results appeared to be representative of

the expected carbohydrate composition. Compared to the hydrolysis of pulp for the HPLC analysis, the conditions are different, in terms of the sulfuric acid concentrations, reaction times, and temperatures. This preparation method was adapted also for time saving reasons. However, the results (see section 3.1) show similar trends as for the HPLC analysis.

A known pulp mass equivalent to approximately 0.5 g was placed in a 50 mL glass bottle and 16 mL of 72% H₂SO₄ was added. The slurry was stirred with magnetic agitation for 2 h at around 25°C. Then, 21 mL of deionized water was added and the bottles were sealed and transferred to a water bath at 80°C for 1 h. The bottles were allowed to cool to room temperature.

The NMR measurements were performed at 10°C with a Varian 500 spectrometer (500 MHz ¹H frequency). The ¹H spectra were acquired with a spectral width of 16 ppm, 90° pulse angle, 2.048 s acquisition time and the relaxation delay was set to 2 s. The data were processed in TOPSPIN v3.1 from Bruker. 600 μL of the hydrolyzed sample was transferred to a NMR tube and 60 μL of a standardizing solution was added, see [36]. After the measurement, the C1-α and C1-β peaks of the sugars were integrated, using the anomeric (α/β) ratio, according to Robyt [37].

2.6 Physical strength properties of the handsheets

Handsheets from pulp without additional xylan—reference sample—and after adsorption were made with a Rapid-Köthen sheet former (*DIN EN ISO 5269-2:2004*). Two different adsorption conditions (low: IS = 1 mol L⁻¹, XC = 8%; high: IS = 2 mol L⁻¹, XC = 32%) were chosen for the softwood kraft pulp. In case of the sulfite pulp only one adsorption condition was investigated (IS = 1 mol L⁻¹, XC = 4%). The other variables were kept constant (T = 80°C, t = 1 h, pH = 7 and 2.5% pulp consistency). After adsorption the pulp was washed to remove free and unbound xylan from the suspension. Then, the fibers were refined in a PFI mill (*ISO 5264-2:2011*) at 1.000 and 3.000 revolutions. Handsheets were made and conditioned (*DIN EN 20187:1993*) before the tensile index and stretch at break (*ISO 1924-2:2008* and *ISO 1924-3:2005*) and also the tear index (*DIN EN 21972:1998*) were determined.

2.7 Pulp and suspension properties

The impact of xylan on the swelling behavior of the modified and unmodified pulp samples was analyzed by measuring the water retention value (WRV). Another focus was the determination of the influence of xylan on the fiber charge and charge density of the pulp by quantifying the surface and total charge as well as the zeta potential.

2.7.1 Fiber charge

The surface and total charge of unrefined pulp samples with and without additional xylan were determined.

The total charge was analyzed by conductometric titration, according to Katz et al. [38]. First, the pulp was transferred to its hydrogen form by using 1 mol L⁻¹ of HCl until the pH was 2.00 ± 0.01 and kept constant for 30 min, as described by Horvath et al. [39, 40]. Subsequently, the pulp was washed with deionized water until the conductivity was below 5 $\mu\text{S cm}^{-1}$. The polyelectrolyte adsorption was carried out similar to the method developed by Winter et al. [41]. Before the titration, a certain amount of NaCl and HCl, both 0.01 mol L⁻¹, were added to minimize the effect of a Donnan equilibrium. After the procedure, the pulp was removed from the suspension and dried, in order to determine the dry weight.

For the analysis of the surface charge, the pulp was first transferred from its hydrogen form to its sodium form by using 1 mmol L⁻¹ of NaHCO₃ and 1 mol L⁻¹ NaOH until the pH was 9.00 ± 0.01 , kept constant for 30 min [39] and washed with deionized water until the conductivity was below 5 $\mu\text{S cm}^{-1}$. A certain amount of polydiallyldimethylammonium chloride (polyDADMAC) was added and stirred for 30 min. Afterwards, the fibers were separated from the suspension and dried, in order to analyze the dry weight. The filtrate was titrated to measure the amount of polyelectrolyte adsorbed on the fiber surface, according to Terayama [42].

2.7.2 Zeta potential

For the determination of the zeta potential the measurement device Müték SZP 04 was used. Therefore, the streaming potential of the liquid phase was acquired, passing the surface of the fibers, due to a back pressure. The fibers were mixed in supply water with a conductivity of 500 $\mu\text{S cm}^{-1}$ to a pulp consistency of 0.3%. Before the analysis, the suspension was allowed to form a shot plug of fibers at the wire for 30 s.

2.7.3 Water retention value

The water retention value (WRV) of the softwood pulp samples was analyzed according to *ISO 23714:2007*. In case of the sulfite pulp, the time during the hydro-extraction was reduced to 15 min.

3 RESULTS AND DISCUSSION

3.1 Chemical analysis of the pulp samples

The xylan content of the softwood kraft pulp was increased due to adsorption. The amount of redeposited xylan on the fibers depends on the adjustment of the six investigated variables. The findings of the determination by HPLC and ¹H NMR spectroscopy are represented in Table 4, where the conditions of the experiments are shown in the left columns and in the right columns the total amount of xylan of the softwood kraft pulp samples before and after adsorption are represented. Both measurement methods, HPLC and ¹H NMR showed a similar development of the amount of xylan on the fibers after

Table 4. Comparison of the results of the total amount of xylan of the softwood kraft pulp samples before and after adsorption trials, determined by HPLC and ¹H NMR spectroscopy

Unit	Conditions						Measurement method				
	C	IS	pH	t	T	XC	HPLC		¹ H NMR		
	%	M	–	h	°C	%	Amount of xylan of the fibers, %				
RS	–	–	–	–	–	–	8.48		8.42		
	2.5	0.25	12.6	1	80	–	7.45		7.85		
Adsorption experiments	<i>with additional xylan</i>						X1	X2	X1	X2	
	1.0						12.49	11.57	11.85	11.09	
	5.0	0.25	7	1	80	16	13.65	11.97	12.34	10.93	
	10						13.48	12.02	13.53	11.20	
	2.5	0.25						13.40	12.07	12.61	11.64
		1	2	7	1	80	16	14.71	13.58	13.58	12.50
	2.5			7				14.84	14.72	14.72	14.28
		0.25		10	1	80	16	13.40	12.07	12.61	11.64
	2.5			12.6				12.76	12.36	12.12	12.01
								10.32	9.81	10.52	10.07
	2.5				0.5			12.82	11.96	11.56	11.32
				7	1	80	16	13.40	12.07	12.61	11.64
	2.5				2			13.46	12.42	14.24	11.22
						40		10.39	10.06	10.42	10.35
2.5			7	1	80	16	13.40	12.07	12.61	11.64	
					140		13.25	13.57	13.39	13.49	
2.5						8	12.65	12.00	11.43	11.59	
	0.25		7	1	80	16	13.40	12.07	12.61	11.64	
2.5						32	17.42	14.61	16.17	14.56	

adsorption experiments. Differences in the values could be explained by the unequal procedures during the hydrolysis, but also by the measurement method itself.

The reference sample (RS) of the softwood pulp showed a xylan content of about 8.5%. The amount of xylan of the reference sample is decreasing by increasing the temperature and the dwell time at a higher temperature level. The dissolution of xylan can also be strengthened by bringing the pH to an alkaline level. Nevertheless, adding additional xylan to the pulp suspension will result in a higher xylan content of the fibers, due to precipitation.

The temperature had a significant influence on adsorption. The amount of X2 could be continuously enhanced by raising the temperature from 40°C to 140°C. In case of X1, no difference was seen between 80°C and 140°C. This may be due to an equilibrium between adsorption and dissolution of xylan. Except for the conditions at 140°C the xylan content of the fibers was higher by adding X1 to the pulp suspension than X2. This means that the deposition of X1 proceeds faster and in case of X2 higher values of the variables need to be adjusted to reach the same increase in xylan content. Thus, the molecular weight of xylan (see Table 2) has an influence on the deposition which could be a result of a higher steric repulsion between bigger and longer aggregates/agglomerates and cellulose. Moreover, X1 has a higher content of MeGlcA (see Table 1). Therefore, stronger interactions can be induced between xylan and the fiber surface. However, a larger amount of MeGlcA has an influence on the solubility of xylan. Higher temperatures, especially under alkaline conditions, will affect the chemical structure by splitting off MeGlcA. Consequently, a reduction of the solubility of xylan follows. This will promote precipitation of xylan on the surface of the fibers [29]. This means in case of X1, that more dissolved xylan can adsorb on the fiber surface, since the content of MeGlcA is higher. Nevertheless, the temperature dependence of adsorption could be due to the decrease in surrounding water forming hydrogen bonds by thermal vibration, allowing an intimate contact between the hydroxyl groups of xylan and cellulose [26, 28].

The pH is important for an efficient xylan precipitation. Lowering the pH from 12.6 to 10 showed an increase in deposition, whereas a further reduction to a neutral pH range brings no further improvement. Hydroxyl groups have a low acid strength ($pK_a = 14$ at 25°C), meaning these groups are ionized only in a strong alkaline environment. A decrease in the pH to a neutral level results in lower solubility of xylan and electrostatic repulsion and is favorable for the precipitation on the fiber surface [43]. Besides the pH value, the ionic strength should be increased. The maximum xylan adsorption was reached with the highest ionic strength. Cellulose and xylan show similar surface textures of hydroxyl groups, indicating likewise surface charges. Moreover, xylan contains carboxyl groups. Therefore, the ionic strength should be high enough to diminish

Table 5. Conditions with highest xylan adsorption onto softwood kraft fibers

<i>Variable</i>	<i>Unit</i>	<i>X1</i>	<i>X2</i>
C	%	10	10
IS	mol L ⁻¹	2	2
pH		7–10	7–10
t	h	0.5	0.5
T	°C	80	140
XC	%	32	32

electrostatic and steric repulsion between xylan molecules, and between xylan and cellulose. In addition, it promotes interactions and associations between these interfaces [29, 34, 44].

Table 5 shows the laboratory conditions with the highest xylan adsorption. In addition, a high xylan concentration and pulp consistency is favorable for a high amount of deposition. From the results, a possible site of xylan addition in the mill could be during an oxygen bleaching sequence, where a sufficient reaction time and temperature level are given.

The amount of adsorbed xylan also seems to be a function of the availability of xylan in the liquid phase. With increasing xylan content in the suspension, the amount of xylan of the fibers was promoted, as can be seen in Figure 1. In case of

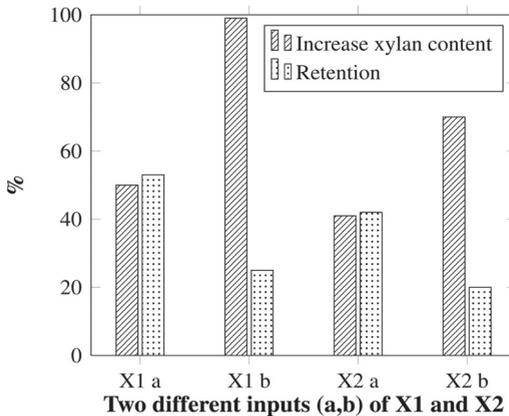


Figure 1. Relationship between the increase in xylan content of the softwood kraft fibers, compared to the reference sample, and the retention of xylan, based on the input, at constant adsorption conditions, only varying the input of xylan. Input: a) XC = 8%; b) XC = 32%.

X1, the amount of xylan of the pulp was around 50% higher compared to the reference pulp at an input of xylan of 8%, based on the dry weight of the fibers. Increasing the input of X1 to 32%, resulted in a nearly 100% higher xylan content, than for the reference sample, while the retention of added xylan was decreasing significantly.

3.2 Physical strength properties of the handsheets

Both xylans had a significant influence on the strength properties of the softwood kraft handsheets and contribute to the mechanisms of bonding within the fiber network. The unrefined pulp samples showed an increase in the tensile strength of 13% with additional X2, compared to the reference sample. The mechanical treatment of the pulp had a higher influence on the handsheets with additional xylan. After beating at 3.000 revolutions with the PFI mill, the maximum increase in tensile index was 28% (X1) and 38% (X2), compared to the reference sample. The results are shown in Figure 2. The coefficient of variation reaches from 2% to 7%.

The molecular weight of the xylan has an impact on the tensile strength of the softwood kraft handsheets, since higher values are achieved with X2. The amount of additional X1 has to be around four times higher, in order to reach a similar tensile strength. Furthermore, the amount of xylan on the cellulose surface is

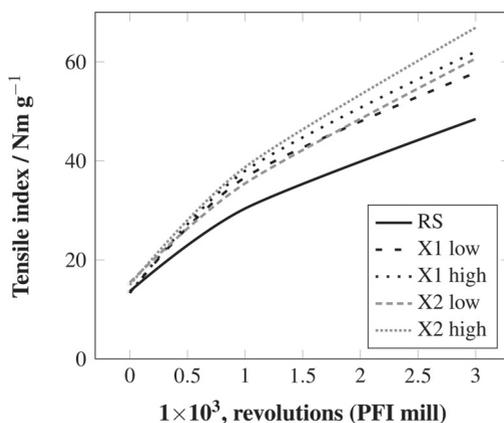


Figure 2. Trend of the tensile index of xylan-modified and unmodified softwood kraft handsheets. Conditions: low) IS = 1 mol L⁻¹, XC = 8%; high) IS = 2 mol L⁻¹, XC = 32% (see section 2.6).

important. By increasing the xylan content of the softwood fibers, the tensile strength is improved.

On the other hand, X1 seems to bring no significant advantage to the tensile strength of the sulfite pulp samples. The tensile index of xylan-modified sulfite pulp handsheets only increased up to nearly 6% compared to the RS beaten at 3.000 revolutions with the PFI mill.

However, the mechanical treatment of pulp leads to more flexible and softer fibers, due to internal and external fibrillation, but also to the production of fines and fiber cutting [45]. Refining always has an impact on the drainage resistance (*ISO 5267-1:1999*) of the pulp, which is increasing by raising the refining energy. Looking at the xylan-modified sulfite pulp, the drainage resistance increased faster than the reference sample at a given refining energy (e.g. 5 SR higher at 3.000 revolutions with a PFI mill). This implies that the xylan-modified pulp samples have a lower refining resistance, which results in enhanced internal and external fibrillation, leading to a larger swelling behavior of the fibers. Further, a higher production of fines could be generated by cutting fibrils and adsorbed xylan off from the fiber surface, as well as a stronger reduction in fiber length. The overall result is a denser and less opaque paper with a higher internal bond (*TAPPI 569 om-09*), compared to the unmodified handsheets.

Comparing kraft and sulfite pulps, the refining resistance of sulfite fibers is in generally lower. The chemical decomposition of lignin in the sulfite process starts from the fiber surface in direction to the lumen, whereas in the kraft process it takes place the opposite way. This leads to a completely dissolved primary cell wall and a strongly affected secondary cell wall in sulfite fibers [1]. Therefore, the fiber surfaces from these pulping methods have different characteristics. The result of beating is a faster increase in fiber flexibility, but also in fines concentration and fiber cutting. This may be a reason for the lower effect of xylan on paper strength of the sulfite handsheets, as more fines may be generated at a given refining energy. On the other hand, the amount of xylan, added to the pulp suspension, was only 4% for the sulfite pulp, whereas for the softwood kraft pulp 8% and 32% of xylan were added. This will affect the mechanical strength properties of the handsheets, since less xylan is involved in the binding mechanisms (cf. Figure 2). In case of the unrefined sulfite pulp, the xylan content of the fibers could be increased from 5.2% to 6.6%—determined by HPLC—due to adsorption. This shows, that the resulting amount of xylan of the sulfite fibers is significantly lower than for the softwood kraft pulp. A result could be a harder sulfite fiber, by reason of a reduced swelling behavior (detailed explanation in section 3.3). Consequently, the surface may have a lower penetration hardness. This will affect the area in molecular contact between adjacent fibers. The penetration hardness of the fiber surface can be analyzed

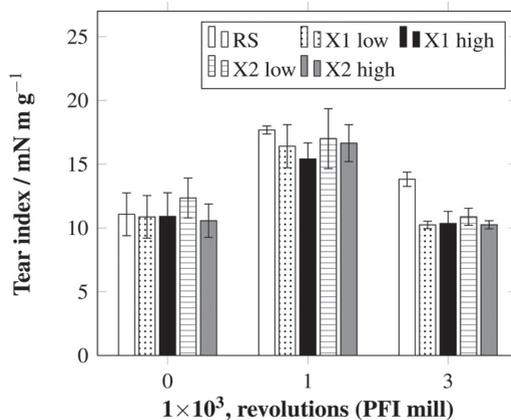


Figure 3. Trend of the tear index of xylan-modified and unmodified softwood kraft handsheets. Conditions: low) IS = 1 mol L⁻¹, XC = 8%; high) IS = 2 mol L⁻¹, XC = 32% (see section 2.6).

by atomic force microscopy and nanoindentation, as described by Persson et al. [46]. Furthermore, the properties and conditions of the fiber surface are different between sulfate and sulfite pulp and could affect the conditions for the precipitation of xylan onto the fibers. These factors will have an influence on the resulting tensile strength of the paper.

Nevertheless, a higher production of fines, due to refining, may also play a role for the xylan-modified softwood kraft pulp, compared to the reference sample. Moreover, an enhanced fines concentration will affect the effective fiber length of the pulp. When a critical fiber length is reached, the mechanical properties of the paper are reducing. This can be seen in Figure 3, where the tear index of the softwood handsheets are represented. The tear index is first increasing (1.000 revolutions) and with longer refining, the values are decreasing. The modified handsheets show a faster dropping down of the tear index at 3.000 revolutions. The reason is a stronger reduction in the effective fiber length of the softwood kraft pulp.

3.3 Fiber charge and zeta potential of the fibers

The pulp samples with additional xylan showed higher values for the surface and total charge, as can be seen in Figure 4. Both, X1 and X2 increased the total charge of the pulp by ~20% from 37.6 µeq/g to about 45 µeq/g. The increase

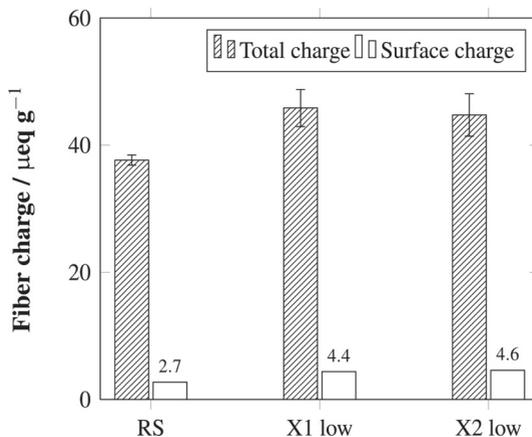


Figure 4. Trend of the total and surface charge of unrefined, xylan-modified and unmodified softwood kraft pulp.

in surface charge was over 60% from 2.72 $\mu\text{eq/g}$ to 4.38 $\mu\text{eq/g}$ (X1) and 4.59 $\mu\text{eq/g}$ (X2).

A higher surface charge and charge density implies that stronger coulomb forces can be achieved by the addition of cations between two negatively charged fibers. Moreover, xylan has an amorphous structure and is able to absorb water, resulting in swelling. This leads to more flexible fibers and brings also a jellylike character to the xylan (hydrogel). These parts are softer on the fiber surface and within the cell wall. Thus, higher and homogeneous areas in molecular contact can be achieved between two adjacent fibers and additional van der Waals forces as well as hydrogen bonds can be generated [46, 47]. This will result in stronger fiber-fiber bonds.

The zeta potential indicates a similar trend. It is increased for the unrefined samples by 1 mV to 3 mV, except for the X1 at low concentration (Table 6).

Table 6. Trend of the zeta potential of xylan-modified and unmodified, unrefined softwood kraft pulp. Conditions: low) IS = 1 mol L⁻¹, XC = 8%; high) IS = 2 mol L⁻¹, XC = 32% (see section 2.6)

	RS	X1 low	X1 high	X2 low	X2 high
Zeta potential in mV	-18.0	-17.0	-20.0	-19.1	-19.9

3.4 Water retention value of the pulp samples

A higher surface charge and charge density of the cellulose surface will lead to stronger swelling behavior. This can be seen in the trend of the water retention value (Figure 5). The WRV of the softwood kraft pulp samples with additional X2 increased faster, compared to the reference sample and to the pulp with additional X1. In case of the sulfite pulp, X1 increases the WRV from 1.27 g g^{-1} (RS) to 1.31 g g^{-1} . Here, the time was reduced from 30 min to 15 min for the centrifugation, due to the generation of heat within the centrifuge. This may have an influence on the results.

Further investigations have to be made, to analyze the influence of X1 on the WRV on the softwood kraft pulp.

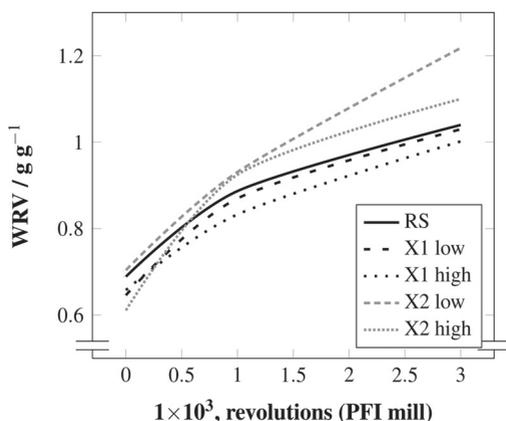


Figure 5. Trend of the water retention value of xylan-modified and unmodified softwood kraft pulp. Conditions: low) IS = 1 mol L^{-1} , XC = 8%; high) IS = 2 mol L^{-1} , XC = 32% (see section 2.6).

4 CONCLUSIONS AND OUTLOOK

The results showed an increase in xylan content due to adsorption. This leads to an enhanced charge density and swelling behavior of the fibers and a higher tensile strength of the paper. However, it is still not clearly understood, whether xylan is adsorbed on the fiber surface forming a film, or also able to diffuse into the pores and the fiber wall.

First results, determined by attenuated total reflectance (ATR) spectroscopy, suggest, that adsorbed xylan is irregularly distributed on the fiber surface.

Nevertheless, this has to be verified with X-ray photoelectron spectroscopy (XPS), low voltage scanning electron microscopy (LV SEM) and atomic force microscopy (AFM) using functionalized tips. Moreover, the influence of xylan on the bonding mechanisms and strength properties of single fiber-fiber joints will be analyzed, according to Fischer et al. [48]. Further investigations with the sulfite pulp have to be made.

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REFERENCES

1. H. Sixta. **Handbook of Pulp**, volume 1 and 2. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2006.
2. A. Jacobs, P.T. Larsson, and O. Ddahlman. Distribution of uronic acids in xylans from various species of softand hardwood as determined by MALDI mass. *Biomacromolecules*, **2**:979–990, 2001.
3. D. Fengel and G. Wegener. Polyoses (hemicelluloses). Ch. 5. **Wood chemistry, ultrastructure and reactions**. Kessler Verlag, 2003.
4. A. Ebringerova, Z. Hromadkova, and T. Heinze. Hemicellulose. *Adv Polym Sci*, **186**:1–67, 2005.
5. H.D. Wilder and E.J. Daleski Jr. Delignification rate studies, part II of a series on kraft pulping kinetics. *Tappi J*, **48**(5):293–297, 1965.
6. T.N. Kleinert. Mechanisms of alkaline delignification. i. the overall reaction pattern. *Tappi J*, **49**(2):53–57, 1966.
7. T.A. Bhaskaran and A. von Koeppen. The degradation of wood carbohydrates during sulphate pulping. *Holzforschung*, **24**(1):14–19, 1970.
8. E. Eriksson and O. Samuelson. Isolation of hemicellulose from sulfite cooking liquors, part 1, acid sulfite cooking. *Sven Papperstidn*, **65**(16):600–605, 1962.
9. S. Axelsson, I. Croon, and B. Enström. Dissolution of hemicelluloses during sulphate pulping, part 1, isolation of hemicelluloses from the cooking liquor at different stages of birch soda cooking. *Sven Papperstidn*, **65**(18):693–697, 1962.
10. R. Simonson. The hemicellulose in sulfate pulping process, part 1, the isolation of hemicellulose fractions from pine sulfate cooking liquors. *Sven Papperstidn*, **66**(20):836–845, 1963.
11. R. Aurell and N. Hartler. Kraft pulping of pine, part 2, the influence on the charge of alkali on the yield, carbohydrate composition and properties of the pulp. *Sven Papperstidn*, **68**(4):97–102, 1965.

12. B. de Groot, J.E.G. van Dam, and K. van't Riet. Alkaline pulping of hemp wood core: kinetic modelling of lignin, xylan and cellulose extraction and degradation. *Holzforschung*, **49**(4):332–342, 1995.
13. J. Buchert, A. Teleman, V. Harjunpää, and M. tenkanen L. Viikari. Effect of cooking and bleaching on the structure of xylan in conventional pine kraft pulp. *Tappi J*, **78**(11):125–130, 1995.
14. A. Jacobs and O. Dahlman. Characterization of the molar masses of hemicelluloses from wood and pulps employing size exclusion chromatography and matrix-assisted laser desorption ionization time-of-flight mass spectrometry. *Biomacromolecules*, **2**(3):894–905, 2001.
15. S. Danielsson and M.E. Lindström. Influence of birch xylan adsorption during kraft cooking on softwood pulp strength. *Nord Pulp Pap Res J*, **20**(4):436–441, 2005.
16. A. Wigell, H. Brelid, and H. Theliander. Degradation/dissolution of softwood hemicelluloses during alkaline cooking at different temperatures and alkalic concentration. *Nord Pulp Pap Res J*, **22**(4):488–494, 2007.
17. R. Aurell. The effect of lowered pH at the end of birch kraft cooks. *Sven Papperstidn*, **66**(11):437–442, 1963.
18. R. Aurell. Increasing kraft pulp yield by redeposition of hemicelluloses. *Tappi J*, **48**(2):80–84, 1965.
19. E.F. Walker. Effects of the uronic acid carboxyls on the sorption of 4-omethylglucuronarabinoxylans and their influence on papermaking properties of cellulose fibers. *Tappi J*, **48**(5):298–303, 1965.
20. Z.L. Jansson and E. Brännvall. Characterisation of dissolved spruce xylan in kraft cooking. *Nord Pulp Pap Res J*, **26**(4):380–385, 2011.
21. B. Leopold and D.C. McIntosh. Chemical composition and physical properties of wood fibers. iii. tensile strength of individual fibers from alkali extracted loblolly pine holocellulose. *Tappi J*, **44**(3):235–240, 1961.
22. C. Schönberg, T. Oksanen, A. Suurnäkki, H. Kettunen, and J. Buchert. The importance of xylan for the strength properties of spruce kraft pulp fibres. *Holzforschung*, **55**(6):639–644, 2001.
23. O. Dahlman, J. Sjöberg, U.B. Jansson, and P.O. Larsson. Effects of surface hardwood xylan on the quality of softwood pulps. *Nord Pulp Pap Res J*, **18**(3):310–315, 2003.
24. J. Sjöberg, M. Kleen, O. Dahlman, R. Agnemo, and H. Sundvall. Fiber surface composition and its relations to papermaking properties of soda-anthraquinone and kraft pulps. *Nord Pulp Pap Res J*, **19**(3):392–396, 2004.
25. S. Yllner and B. Enström. Studies of the adsorption of xylan on cellulose fibres during the sulphate cook, part 2. *Sven Papperstidn*, **60**(15):549–554, 1957.
26. N. Hartler and A. Lund. Sorption of xylans on cotton. *Sven Papperstidn*, **65**:951–955, 1962.
27. D.W. Clayton and J.E. Stone. The redeposition of hemicelluloses during pulping. part i. the use of a tritium-labelled xylan. *Pulp Pap Mag Canada*, **64**:T459–T468, 1963.
28. J.Å. Hansson. Sorption of hemicelluloses on cellulose fibres, part 3, the temperature dependence on sorption of birch xylan and pine glucomannan at kraft pulping conditions. *Sven Papperstidn*, **73**(3):49–53, 1970.

29. M. Mittika-Eklund. Sorption of xylans on cellulose fibres, Licentiate thesis. Department of Forest Products Technology, Helsinki University of Technology, 1996.
30. Å. Henriksson and P. Gatenholm. Controlled assembly of glucuronoxylans onto cellulose fibers. *Holzforschung*, **55**(5):494–502, 2001.
31. P. Westbye, C. Svanberg, and P. Gatenholm. The effect of molecular composition of xylan extracted from birch on its assembly onto bleached softwood kraft pulp. *Holzforschung*, **60**:143–148, 2006.
32. T. Köhnke. Adsorption of xylans on cellulosic fibres, influence of xylan composition on adsorption characteristics and kraft pulp properties. PhD thesis, Department of Chemical and Biological Engineering, Chalmers University of Technology, Göteborg, 2010.
33. M.C. dos Santos Muguet, C. Pedrazzi, and J.L. Colodette. Xylan deposition onto eucalyptus pulp fibers during oxygen delignification. *Holzforschung*, **65**:605–612, 2011.
34. Å. Linder, R. Bergman, A. Bodin, and P. Gatenholm. Mechanism of assembly of xylan onto cellulose surfaces. *Langmuir*, **19**(12):5072–5077, 2003.
35. H. Sixta, N. Schelosky, W. Milacher, T. Baldinger, and T. Röder. Characterization of alkalisoluble pulp fractions by chromatography. In *proc. 11th International Symposium on Wood and Pulping Chemistry*, pages 655–658, Nice, France, 2001.
36. S.B. Bose, V.A. Barber, E.F. Alves, D.J. Kiemle, and A.J. Stipanovic. An improved method for the hydrolysis of hardwood carbohydrates to monomers. *Carbohydr Polym*, **78**:396–401, 2009.
37. J.F. Robyt. *Essentials of carbohydrate chemistry*. Springer-Verlag New York, Inc., 1998.
38. S. Katz, R.P. Beatson, and A.M. Scallan. The determination of strong and weak acidic groups in sulfite pulps. *Sven Papperstidn*, **87**(6):R48–R53, 1984.
39. A.E. Horvath, T. Lindström, and J. Laine. On the indirect polyelectrolyte titration of cellulosic fibers. conditions for charge stoichiometry and comparison with esca. *Langmuir*, **22**(2):824–830, 2006.
40. A.E. Horvath and T. Lindström. Indirect polyelectrolyte titration of cellulosic fibers – surface and bulk charges of cellulosic fibers. *Nord Pulp Pap Res J*, **22**(1):87–92, 2007.
41. L. Winter, L. Wågberg, L. Ödberg, and T. Lindström. Polyelectrolytes adsorbed on the surface of cellulosic materials. *J Colloid Interf Sci*, **111**(2):537–543, 1985.
42. H. Terayama. Method of colloid titration (a new titration between polymer ions). *J Polym Sci*, **8**(2):243–253, 1952.
43. E. Sjöström. The origin of charge on cellulose fibers. *Nord Pulp Pap Mag Canada*, **4**:90–93, 1989.
44. G. Ström, P. Barla, and P. Stenius. The effect of pine xylan on the use of some polycations as retention and drainage aids. *Sven Papperstidn*, **85**(12):R100–R106, 1982.
45. R.J. Kerekes. Characterization refining action in PFI mills. *Tappi J*, **4**(3):9–14, 2005.

46. B.N.J. Persson, C. Ganser, F. Schmied, C. Teichert, R. Schennach, E. Gilli, and U. Hirn. Adhesion of cellulose fibers in paper. *J Phys*, **25**(4):1–11, 2013.
47. A. Torgnysdotter, A. Kulachenko, P. Gardin, and L. Wågberg. The link between the fiber contact zone and the physical properties of paper: a way to control paper properties. *J Compos Mater*, **41**(13):1619–1633, 2007.
48. W.J. Fischer, U. Hirn, W. Bauer, and R. Schennach. Testing of individual fiberfiber joints under biaxial load and simultaneous analysis of deformation. *Nord Pulp Pap Res J*, **27**(2):237–244, 2012.

Transcription of Discussion

IMPROVEMENT OF PAPER STRENGTH BY INCREASING THE XYLAN CONTENT

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Lars Wågberg KTH

I have two questions. The first one is, when you lower the pH or increase the temperature, do you have any feeling for how the solution properties, or the xylan, is changed? Does it precipitate, and what is the size of the precipitates?

Albrecht Miletzky

Well, the solution is getting turbid, so the xylan is precipitating, but we do not know yet about the size distribution of the precipitated xylan.

Lars Wågberg

The second question is, did you plot your results of tensile index as a function of density for the different treatments? Because that would be really interesting.

Discussion

Albrecht Miletzky

No, we have not done that yet but I will look into it.

Jim De Witt Sappi

Do you see this material as being more effective as a paper mill or a pulp mill additive?

Albrecht Miletzky

Well when you look at the concentration of xylan we added to the pulp, I do not think it is compatible with other chemicals, because it is quite high at around 8 %. I don't have any information about possible costs of such a xylan, but maybe there are some areas where we can add the xylan; in a pulp mill or in the bleaching stage, for example, and you can reduce the energy you need for refining.

Jim De Witt

Does it have an effect on the optical properties or brightness of the pulp?

Albrecht Miletzky

A little bit, yes. When you dissolve the xylan into the sodium hydroxide, it is getting a little bit yellowish-brownish, and that you will see also on the pulp. Brightness is little bit decreased, yes.

Jim De Witt

Do you consider the sodium chloride to be an essential part of putting the xylan onto the pulp?

Albrecht Miletzky

Well, it is not essential, we can also use different salts, but when you increase the ionic strength, it will diminish the electrostatic repulsion between the xylan and cellulose, so it is getting adsorbed more easily.

Jim De Witt

A one molar salt concentration is extremely high, even going through the washing stage, with possible consequences in the paper mill.

Patrick Huber CTP

You mentioned in your introduction that you wanted to recover the xylan from the black liquor, is that correct?

Albrecht Miletzky

Yes, that was done. Lenzing did that for us and we just got the two xylans in powder form.

Patrick Huber

But then, if I understood you correctly, in your work you extracted the xylan from the pulp?

Albrecht Miletzky

One was extracted from cooking liquor, and the other one was extracted from eucalyptus kraft pulp.

Patrick Huber

Okay, so there was one from the liquor and one from the pulp. So could you comment on the difference between those two types of xylan and the implications for your findings?

Albrecht Miletzky

Well one xylan was extracted from the cooking liquor, and the other one was extracted from the pulp, because we wanted to investigate two different xylans. The xylans differed in their molecular weight and chemical composition.

Patrick Huber

I was wondering if you had measured residual lignin bonded to the xylan, in both cases.

Albrecht Miletzky

No, we did not measure the residual lignin of the xylans, but we should check that.

Discussion

Patrick Huber

There should be some.

Harshad Pande Domtar

You said you saw loss of brightness in the handsheets, how much was the loss?

Albrecht Miletzky

We did some adsorption tests with a sulfite pulp from an industry partner and we saw a loss in brightness, I think it was from 85% down to 80%.