

# Modifying cellulose fibers by adsorption/precipitation of xylan

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**Abstract** Xylan was precipitated on bleached and unbleached softwood kraft pulps (SKPB and SKPUB), a bleached sulfite pulp, and viscose fibers to investigate the influence on physical properties of handsheets as well as to gain more detailed information of the distribution of adsorbed xylan on cellulosic surfaces. The adsorption step was carried out at constant conditions. The values of the parameters were chosen after a series of different adsorption steps (as presented elsewhere) also in regard as a possible industrial application. Afterwards, suspension and physical strength properties of unrefined and refined samples

were determined. Refining resulted in a stronger increase in the beating degree of the pulps with additional xylan than the reference samples. The water retention value was not significantly changed. Comparing the tensile index of the handsheets versus the beating degree a remarkable increase in the strength properties was not observed. The investigation of the surface of the SKPB fibers via ATR suggests that precipitated xylan is heterogeneously and nonuniformly distributed. On cellulose model films, particles could be detected via atomic force microscopy. Phase images recorded with OH-functionalized tips suggested that these particles consist of xylan. An

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inhomogeneous distribution of xylan could be a reason that there is no measurable influence on the strength properties of the handsheets.

**Keywords** Xylan adsorption · Xylan distribution · Strength properties · ATR spectroscopy · SEM (conventional and low-voltage mode) · AFM with functionalized tips

## Introduction

Xylan is a native biopolymer found in plants and wood. Hardwoods can contain up to 35 % of xylan (Sixta 2006). Wood xylans exhibit a homopolymer backbone of xylose units, with the monomers are covalently linked by  $\beta$ -(1,4)-glycosidic bonds. In contrast to cellulose, xylans hold a variety of different side groups, such as *O*-methylglucuronic acid residues, *O*-acetyl groups, small amounts of rhamnose and galacturonic acid, or  $\alpha$ -L-arabinofuranose (Ebringerová et al. 2005; Fengel and Wegener 2003; Jacobs and Dahlman 2001), resulting in a rather complex structure.

Within the cell wall matrix of wood fibers, xylan is rather linked to lignin (Lawoko et al. 2004, 2006) and incorporated between the cellulose fibrils. This has an influence on the porous structure (size, amount, and distribution of pores) within the fiber wall (Stone and Scallan 1968) as well as the swelling behavior and wet flexibility of a fiber after pulping (Moss and Pere 2006) since xylan is simultaneously removed with lignin. The reduction of the amount of xylan during pulping, bleaching, or other extracting methods (e.g. enzymatic extraction) leads to a decrease in strength properties (Cao et al. 1998; Leopold and McIntosh 1961; McIntosh 1963; Rauvanto et al. 2006; Schönberg et al. 2001; Sjöberg et al. 2004; Spiegelberg 1966) which is explained by lowering the wet fiber flexibility (Laine and Stenius 1997; Pettersson and Rydholm 1961). Thus, the elastic modulus and consequently the penetration hardness are affected which are decreasing with increasing swelling behavior (Persson et al. 2013). The result is a closer contact between adjacent fibers provoking a larger area in molecular contact during sheet formation as the fibers are softer and more flexible. However, a higher degree of swelling is affecting the water removal during the network formation adversely.

Therefore, the addition of xylan onto cellulose fibers is a research field of great interest. The addition of cationic xylan had a positive effect on the tear resistance and other physical strength properties on various pulp samples, as it acted as a retention aid (Antal et al. 1997; Ren et al. 2009), but also increased the refining resistance (Antal et al. 1991). Köhnke et al. (2008) recognized an improved tensile index of the pulp after a treatment with arabinoxylan by comparing it with the refining intensity. In relation to the beating degree, no increase in tensile strength of pulp with additional xylan could be observed (Köhnke and Gatenholm 2007).

Henriksson and Gatenholm (2001,2002) detected attached xylan on cellulosic surfaces as bump-like structures in the  $\mu\text{m}$  size range by scanning electron microscopy, whereas (Linder et al. 2003) visualized globular particles in the colloidal size via atomic force microscopy. Contrary to these findings, the deposition of xylan occurred with different patterns (Coleho dos Santos Muguet et al. 2011), forming net-like structures between fibers (Silva et al. 2011).

The impact of adsorbed/precipitated xylan on the strength properties of pulps and their shape on the fiber surface is controversially discussed in the literature. Therefore, the influence of additional xylans on physical properties of various pulp samples was studied in this paper. The distribution of precipitated xylan on softwood kraft pulp fibers was determined by attenuated total reflection (ATR) spectroscopy as well as scanning electron microscopy (SEM) in the conventional and low-voltage mode (LVSEM). In addition, atomic force microscopy (AFM) was performed using OH-functionalized tips to analyze the shape and size of attached xylan on the surface of cellulose model films as well as the adhesive forces.

## Materials and methods

### Pulp preparation

Different unrefined fiber samples were used:

1. once-dried, bleached softwood kraft pulp (SKPB) (Mondi),
2. two never-dried, unbleached softwood kraft pulps (SKPUBs) with a Kappa number of 54 and 42 (Mondi),

3. once-dried, bleached sulfite pulp (SPB) (Sappi Paper Holding GmbH, Gratkorn), and
4. flat viscose fibers (VF) with a fiber length of 6 mm and a titer of 9 dtex (Kelheim Fibres GmbH).

Dry SKPB (bale form) was soaked in deionized water for at least 4 h and disintegrated for 25 min (ISO 5263-2:2004). The pulp was thickened to a dry content of about 20 % and stored in a refrigerator until use. The same procedure was applied to the SPB (sheet form). Only the time for the disintegration was reduced to 10 min (ISO 5263-1:2004). The never-dried SKPBs were already disintegrated and had a dry content of about 20 %. The VFs were first washed in a laboratory dyeing apparatus Labomat Mathis (Switzerland), with metal cuvettes in which the VFs were weighed and the standard soap solution with a concentration of 5 g L<sup>-1</sup>, (pre-heated to 60 °C) were added, considering the bath ratio of 1:50. One washing cycle was carried out for 30 min at 60 °C and the frequency of rotation of the cuvettes was 40 min<sup>-1</sup>. This was done in order to remove possible additives from the surface. Before use, the VFs were soaked in deionized water for at least 4 h.

### Xylan preparation

Two different xylans (powder form) were used for the adsorption and were provided by Lenzing AG. Xylan 1 (X1) was extracted from a beech sulfite dissolving pulp and xylan 2 (X2) from eucalyptus kraft pulp. The molecular weight (weight average; determined by size-exclusion technique) of X2 (17.9 kDa) was almost twice as high as that of X1 (9.0 kDa). The xylose content was about 90 % for both xylans, whereas X1 had a higher content of uronic acid residues of about 4.8 %, compared to 3.7 % for X2. Furthermore, X1 had a small amount of mannose (0.4 %) and X2 consisted of 0.4 % galactose. In both xylans, a small amount of glucose of 0.8 % (X1) and 0.2 % (X2) was present. The chemical composition was determined via gas chromatography.

The xylans were added to sodium hydroxide solution (NaOH) (1 mol L<sup>-1</sup>) and stirred for 15 min (X1) and 25 min (X2), and heated to about 55 °C for dissolution. However, bigger parts of X2 remained as solid parts. Before use, the solution was cooled to room temperature.

### Adsorption experiments

In this study, the temperature (80 °C), adsorption time (1 h), pH (7), ionic strength (1 mol L<sup>-1</sup>), pulp consistency (2.5 %), and xylan concentration (8 %) were kept constant. The values were chosen according to Miletzky et al. (2013). The adsorption conditions in this paper were chosen such that the amount of xylan could be significantly increased. This was also done with respect to possible sites of xylan addition in the mill. Three different values of these variables were studied (Miletzky et al. 2013).

First, the thickened pulp sample was put into an Erlenmeyer flask. NaCl was dissolved in deionized water to set the ionic strength to 1 mol L<sup>-1</sup>. The water was added to the pulp and the suspension was mixed in order to separate the fibers. The xylan solution was added to the suspension and the pH was carefully adjusted to seven using sulfuric acid. Then, the flask was sealed with a stopple and a bail, and placed in a heated water bath at 80 °C. After the adsorption time of 1 h with respect to the heating period, the pulp was washed with deionized water until the conductivity was below 10 µS cm<sup>-1</sup>. The same procedure was performed with the reference sample, except the addition of xylan.

### Chemical analysis of the pulp

The chemical composition of the fiber samples, before and after the adsorption procedure was analyzed via high-pressure liquid chromatography (HPLC). Before the analysis, the pulp samples were milled, dissolved, and degraded to their neutral sugar monomers in a two-stage hydrolysis by sulfuric acid, according to Sixta et al. (2001).

A known pulp mass equivalent to 40 mg was placed in a 10 mL centrifuge tube and 0.5 mL of 72.3 % H<sub>2</sub>SO<sub>4</sub> was added. The slurry was stirred for 3.5 h at 25 °C. Then, 8.5 mL of deionized water was added, the tubes were sealed, and placed in a heatable rotator at 110.0 ± 0.1 °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 % of NaOH (w/w) 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 and hydroxymethylfurfural

which is formed during the degradation of xylan and glucan. Afterwards, the samples were transferred to a cuvette and analyzed. The sugar monomers were separated by a CarboPac<sup>TM</sup> PA10 column (4 × 250 mm from Dionex). The detection of the monomers was accomplished with pulsed amperometric detection (Dionex ED40).

### Strength properties

The pulp was washed to remove free and unbound xylan as well as the NaCl from the suspension (section “[Adsorption experiments](#)”). Then, the fibers were refined in a PFI mill (ISO 5264-2:2011) at 1,000 and 3,000 revolutions. Handsheets were made with a Rapid-Köthen sheet former (DIN EN ISO 5269-2:2004) and conditioned (DIN EN 20187:1993) before the tensile index (ISO 1924-2:2008) and the tear index (DIN EN 21972-2:1998) were determined.

### Suspension properties

The beating degree (ISO 5267-1:2002) and the water retention value (ISO 23718:2007) of the pulp samples were determined. Before the analysis, the conductivity was set to 500  $\mu\text{S cm}^{-1}$  using a solution of KCl. Further, the surface and total charge of unrefined, heat-treated SKPB with and without dissolved NaCl was measured. The results of the charge density of the unrefined SKPB and the SKPB with additional xylan were presented elsewhere (Miletzky et al. 2013).

The total charge was analyzed by conductometric titration, according to Katz et al. (1984). First, the pulp was transferred to its hydrogen form using 1 mol L<sup>-1</sup> of HCl until the pH was  $2.00 \pm 0.01$  and kept constant for 30 min, as described by Horvath et al. (2006) and Horvath and Lindström (2007). 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. (1985). Moreover, NaCl and HCl, both 0.01 mol L<sup>-1</sup>, 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 using 1 mmol L<sup>-1</sup> of NaHCO<sub>3</sub> and 1 mol L<sup>-1</sup> NaOH until the pH was  $9.00 \pm 0.01$ , kept constant for

30 min (Horvath et al. 2006), and washed with deionized water until the conductivity was below 5  $\mu\text{S cm}^{-1}$ . Polydiallyldimethylammonium chlorid was added and the suspension was 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 (1952).

### Infrared spectroscopy

Attenuated total reflection (ATR) spectroscopy was performed on 2 × 2 cm<sup>2</sup> sections of SKPB sheet samples and on the pure xylan samples using an IFS 66 v/S FTIR spectrometer (Bruker), according to Gilli et al. (2009). For the analysis, SKPB fibers were exposed to different xylan concentrations (8 and 32 %) during the adsorption step (section “[Adsorption experiments](#)”). Therefore, the SKPB sheet samples held different amounts of precipitated xylan, as elsewhere presented (Miletzky et al. 2013). A single reflection unit (MKII Golden Gate<sup>TM</sup> from Specac) was used with a diamond as ATR crystal. The incident angle was 45°. A sampling rate of 100 kHz and a recording time of 10 min was used. The spectra were processed in OPUS (Bruker).

Xylan features characteristic peaks at wavelengths of 1,250 and 1,460 cm<sup>-1</sup> as well as at 1,650 and 1,750 cm<sup>-1</sup>, resulting from C=O bond stretching vibration at the COOH groups (Evans et al. 1995; Fengel 1992; Higgins et al. 1961; Kačuráková et al. 1999).

### Scanning electron microscopy

The surfaces of the pulp samples were imaged by SEM. Two approaches were taken:

1. sputter coating using gold for conventional SEM and
2. no sputter coating for low-voltage SEM (LVSEM).

Before sputter coating, SKPB handsheets (with and without additional xylan) were placed in deionized water and mixed in order to separate the fibers from each other. Individual fibers were fixed on carbon tape, and afterwards sputter coating was performed (for 90 s) using gold. A S-4000 (HITACHI) was utilized at an electron energy of 8 keV.

For the investigations via LVSEM pieces of SKPB handsheets (with and without additional xylan) were fixed on carbon tape. The same procedure was applied to individual fibers which were first rewetted in deionized water, separated from the handsheets, and air-dried on the carbon tape. The measurements were performed in an Ultra 55 (Zeiss) at an electron energy of 0.7 keV.

### Atomic force microscopy

Atomic force microscopy was performed in order to verify the results from ATR spectroscopy. An MFP-3D AFM (Asylum Research) was utilized which was equipped with a planar closed-loop scanner and operated in tapping mode. The tips had been functionalized with OH groups (Nanocraft) and had an estimated tip radius of 20–40 nm. The spring constants of the cantilevers were 2–3 N m<sup>-1</sup>. To obtain information on the adhesive interactions between tip and sample, the surfaces were scanned in the repulsive regime.

### Cellulose model film preparation for AFM measurements

Thin cellulose model films were prepared, according to Rohm et al. (2014). Trimethylsilyl cellulose (TMSC) was dissolved (1 wt%) in toluene, and then deposited by spin coating ( $v = 4,000$  rpm,  $a = 2,500$  rpm s<sup>-1</sup>,  $t = 60$  s) onto Si-wafer substrates. Afterwards, the TMSC films were converted in a petri dish into amorphous cellulose (Kontturi et al. 2003; Mohan et al. 2012) by exposure to HCl vapor created by 2 mL of a 10 % HCl solution for 10 min. Some of the regenerated cellulose films were treated with a solution of xylan (0.5 g L<sup>-1</sup>, pH 8, 1 mmol NaCl) at room temperature for 30 min. The solution was obtained by dissolving the xylan (X1) in 1 mol L<sup>-1</sup> NaOH, which was then set to pH 8 by 1 mol L<sup>-1</sup> HCl and NaCl was added. After the treatment, the samples were placed in deionized water for 30 min and dried.

## Results and discussion

### Chemical analysis

After adsorption/precipitation of xylan, the xylan content of the pulp fibers could be increased, as

depicted in Table 1. The attachment of X1 occurs to a higher extend than X2, due to the lower molecular weight. The lower molecular weight of X1 as well as the higher content of uronic acid lead to a higher solubility of xylan. While lowering the pH to a neutral environment, xylan adsorbs as well as precipitates on the surface and agglomerates to larger particles. The undissolved parts could have an effect on the adsorption of soluble xylan molecules but are also able to precipitate on the favorable areas on the fibers surface. Recent QCM-D measurements showed no difference between in the adsorption from clear and turbid solutions. The ionic strength promotes a stronger attraction between xylan and cellulose, as repulsive forces between the hydroxyl and carboxyl groups are reduced (Mittika-Eklund 1996). The solubility of xylan molecules is also dependent on the salt used to set the ionic strength. Ions can either promote or retard the solubility of xylan in aqueous solution (Hofmeister series) and thus, affect precipitation of xylan. It is also possible that xylan enters into the pores of the fiber wall, when the size of the particles is small enough. In addition, the conformation of a polyelectrolyte is strongly influenced by the salt concentration (Dobrynin and Rubinstein 2005; Dobrynin et al. 2001). A higher ionic strength usually leads to coiled like conformations, whereas a lower ionic strength to stretched and flat elongation of polyelectrolytes. Therefore, it could be possible that attached xylan changes its conformation during the washing step.

In comparison to the SKPB fibers, less xylan is adsorbing/precipitating onto the unbleached fibers, but is similar for both SKPUBs. During pulping lignin is becoming more soluble for bleachable grade pulps (Lin 1992) due to the formation of polar groups. Therefore, stronger repulsive forces between xylan and residual lignin can occur. Shigematsu et al. (1994) recognized a higher affinity between cellulose and hemicelluloses than for hemicelluloses and lignin. Furthermore, during chemical pulping, the lignin macromolecules are getting degraded and solubilized to a major extend (Sixta 2006). Therefore, it is possible that fragments are again precipitating on the fiber surface at the end of the cook (Aurell 1963; Schmied et al. 2012) making the fiber surface less attractive to xylan.

The difference between SKPB and SPB is most likely another surface morphology and chemistry,

**Table 1** Chemical composition of the fiber samples before and after adsorption of xylan by HPLC

Sample	Glu (%)	Xyl (%)	Man (%)	Ara (%)	Rha (%)	Gal (%)	KL (%)	SL (%)
SPB	87.5 ± 0.5	5.3 ± 0.0	5.4 ± 0.1	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.06 ± 0.03	1.02 ± 0.01
SPB ht <sup>1</sup> NaCl	86.6 ± 1.0	5.2 ± 0.0	5.4 ± 0.1	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0		
SPB X1	84.3 ± 0.1	7.7 ± 0.1	5.3 ± 0.1	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0		
SPB X2	86.2 ± 0.2	6.6 ± 0.0	5.3 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0		
SKPB	80.5 ± 1.2	7.8 ± 0.1	6.2 ± 0.1	0.5 ± 0.0	0.0 ± 0.0	0.2 ± 0.0	0.22 ± 0.01	0.22 ± 0.01
SKPB ht NaCl	79.3 ± 1.0	7.8 ± 0.1	6.2 ± 0.1	0.5 ± 0.0	0.0 ± 0.0	0.2 ± 0.0		
SKPB X1	77.1 ± 1.2	11.1 ± 0.2	5.9 ± 0.0	0.5 ± 0.0	0.0 ± 0.0	0.2 ± 0.0		
SKPB X2	77.0 ± 1.6	9.4 ± 0.1	6.0 ± 0.1	0.4 ± 0.0	0.0 ± 0.0	0.2 ± 0.0		
SKPUB κ42	77.7 ± 0.4	7.8 ± 0.0	6.1 ± 0.0	0.8 ± 0.0	0.1 ± 0.0	0.5 ± 0.0	6.49 ± 0.06	0.17 ± 0.01
SKPUB κ42 ht NaCl	77.9 ± 0.6	7.7 ± 0.1	6.2 ± 0.0	0.8 ± 0.0	0.1 ± 0.0	0.5 ± 0.0		
SKPUB κ42 X1	76.1 ± 0.8	9.5 ± 0.1	6.0 ± 0.0	0.7 ± 0.0	0.1 ± 0.0	0.5 ± 0.0		
SKPUB κ54	75.2 ± 1.0	7.9 ± 0.1	6.0 ± 0.0	0.8 ± 0.0	0.1 ± 0.0	0.6 ± 0.0	8.04 ± 0.21	0.18 ± 0.01
SKPUB κ54 ht NaCl	75.6 ± 0.9	7.8 ± 0.1	6.0 ± 0.1	0.8 ± 0.0	0.1 ± 0.0	0.6 ± 0.0		
SKPUB κ54 X1	73.4 ± 1.4	9.7 ± 0.1	5.8 ± 0.0	0.8 ± 0.0	0.1 ± 0.0	0.6 ± 0.0		
VF	93.6 ± 0.4	1.2 ± 0.0	0.6 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0		
VF ht	95.0 ± 0.6	1.3 ± 0.0	0.6 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0		
VF ht NaCl	95.3 ± 0.4	1.2 ± 0.0	0.6 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0		
VF X1	95.9 ± 0.4	1.2 ± 0.0	0.6 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0		
VF X2	95.9 ± 1.2	1.2 ± 0.0	0.6 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0		

*Glu* glucose, *Xyl* xylose, *Man* mannose, *Ara* arabinose, *Rha* rhamnose, *Gal* galactose, *KL* Klason lignin, *SL* acid-soluble lignin

<sup>1</sup> *ht* heat-treated. The same adsorption conditions were chosen, but no xylan was added

especially a lower hemicellulose content on the fiber surface (Bachner et al. 1993), resulting from the different cooking conditions.

Viscose fibers were investigated whether they could be used as model fibers, as they consist predominantly of cellulose. However, no adsorption/precipitation of xylan onto the VFs could be detected via HPLC even after washing to purify the surface. On the other hand, xylan did adsorb on the cellulose model films which are built up by cellulose II as well. A reason could be the detection limit of the measurement of the HPLC technique.

### Suspension properties

In Table 2, the development of the water retention value (WRV) and the beating degree of the pulp samples before and after refining is presented. It was observed that the beating degree for the pulp samples with additional xylan increased faster than the reference samples, especially for the SPB which has in

general a lower refining resistance due to the pulping method (Bachner et al. 1993). The WRV does not show a large difference between the samples. Xylan seems to have an influence on the beating resistance, as it is able to bind water which makes the fiber surface soft and more flexible (Köhnke and Gatenholm 2007). Therefore, a higher beating degree can be achieved at the same refining intensity. This could be an advantage in saving energy for the adjustment of the physical properties of pulp during a refining stage.

In a previous study (Miletzky et al. 2013), the total and surface charges of the unrefined SKPB were determined for the reference sample and the samples treated with X1 and X2. The total charge was increased by more than 20 % and the surface charge could be enhanced by 60 %. In this study, the SKPB reference sample was heat-treated in deionized water at 80 °C for 1 h. Further, the same procedure, as described in section “[Adsorption experiments](#)”, was applied to the SKPB reference sample, except no xylan was added. The total and surface charge was not affected by both methods.



**Table 2** Development of the beating degree and the water retention value (WRV) of the different fiber samples

Sample	Beating degree, SR			WRV (g/g)		
	0 PFI	1,000 PFI	3,000 PFI	0 PFI	1,000 PFI	3,000 PFI
SPB	12.8	14.5	24.8	0.908 ± 0.001	1.271 ± 0.005	1.605 ± 0.033
SPB ht NaCl	13.0	15.5	27.3	0.890 ± 0.001	1.272 ± 0.003	1.560 ± 0.017
SPB X1	13.0	16.0	31.0	0.862 ± 0.002	1.260 ± 0.007	1.599 ± 0.004
SPB X2	12.0	15.5	30.0	0.895 ± 0.001	1.269 ± 0.003	1.705 ± 0.042
SKPB	13.2	14.8	17.8	0.834 ± 0.013	1.130 ± 0.002	1.396 ± 0.006
SKPB ht NaCl	12.8	13.3	17.6	0.870 ± 0.003	1.160 ± 0.009	1.377 ± 0.026
SKPB X1	12.8	14.0	20.0	0.890 ± 0.020	1.161 ± 0.036	1.479 ± 0.047
SKPB X2	12.5	13.6	18.8	0.856 ± 0.012	1.114 ± 0.005	1.370 ± 0.033
SKPUB κ42	13.3	14.0	14.8	1.418 ± 0.004	1.381 ± 0.092	1.541 ± 0.010
SKPUB κ42 ht NaCl	13.7	13.8	15.3	1.454 ± 0.003	1.481 ± 0.002	1.596 ± 0.005
SKPUB κ42 X1	14.2	14.0	15.5	1.432 ± 0.008	1.466 ± 0.004	1.611 ± 0.001
SKPUB κ54	13.4	14.6	14.8	1.477 ± 0.144	1.411 ± 0.0029	1.624 ± 0.135
SKPUB κ54 ht NaCl	13.6	14.1	15.0	1.444 ± 0.014	1.488 ± 0.001	1.595 ± 0.002
SKPUB κ54 X1	13.3	13.8	15.0	1.413 ± 0.010	1.473 ± 0.004	1.609 ± 0.003
VF	10.2	–	–	0.712 ± 0.002	–	–
VF ht	10.9	–	–	0.728 ± 0.009	–	–
VF ht NaCl	11.5	–	–	0.720 ± 0.005	–	–
VF X1	11.2	–	–	0.705 ± 0.006	–	–
VF X2	11.3	–	–	0.721 ± 0.012	–	–

0 PFI = 0 revolutions; 1,000 PFI = 1,000 revolutions; and 3,000 PFI = 3,000 revolutions

## Surface analysis

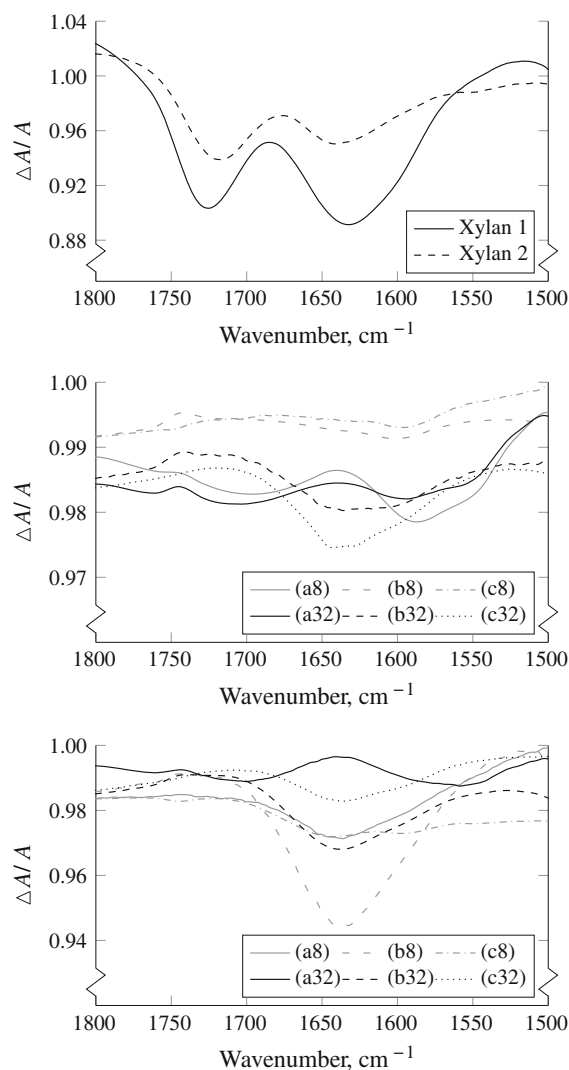
### ATR spectroscopy

Handsheets of SKPB with and without precipitated xylan, unrefined (a) and refined at 1,000 (b) and 3,000 (c) revolutions (PFI mill) were analyzed by ATR spectroscopy in order to determine the intensity of the infrared (IR) peaks at the wavelengths of 1,650 and 1,750  $\text{cm}^{-1}$ . In this region COOH groups show characteristic stretching vibrations. Moreover, it was to prove whether the intensity of the IR peaks is higher for the refined samples. It could be possible that xylan is able to penetrate or diffuse into the pores of the fiber wall and after refining it is getting again accessible on the fiber surface, where it can contribute to the bonding mechanisms between adjacent fibers.

Firstly, both xylans were analyzed in their powder form to determine the intensities of the characteristic IR peaks. X1 shows a larger absorption of IR light between these wavelengths than X2 which is depicted

in Fig. 1 (top). This behavior is due to a higher amount of uronic acid residues, that consist of carboxyl groups, in X1.

The intensities of the IR peaks fluctuate between different refining intensities as well as different amounts of precipitated xylan (X1 and X2) on the SKPB handsheet samples, as illustrated in Fig. 1 (middle and bottom). In the middle, the intensities of (a32) and (b32) are quite similar, whereas the peak at 1,650  $\text{cm}^{-1}$  of (c32) is larger. In the bottom figure, the intensity of (b8) is much larger than for (a8) and (c8) as well as at higher amounts of xylan. Further measurements at other areas of the handsheets resulted in similar fluctuations. Sometimes the IR peaks at a xylan concentration (during the adsorption step) of 8 % were larger than at 32 % and reverse. The variations were also present between unrefined and refined samples. Therefore, no clear trend regarding in the intensities of the IR peaks at an increased amount of adsorbed/precipitated xylan could be observed. This could indicate that xylan is



**Fig. 1** ATR spectra of: *top* pure xylan 1 and xylan 2; *middle* SPKB handsheets with additional X1 (xylan concentration during adsorption: 8 = 8 and 32 = 32 %) at *a* 0, *b* 1,000, and *c* 3,000 revolutions; and *bottom* SPKB handsheets with additional X2 (xylan concentration during adsorption: 8 = 8 and 32 = 32 %) at *a* 0, *b* 1,000, and *c* 3,000 revolutions

nonuniformly and heterogeneously distributed on the fiber surface, even for additional xylan which is in accordance with Henriksson and Gatenholm (2002), Linder et al. (2003).

### SEM

The detection of the surface texture of individual SKPB fibers before and after the treatment with xylan were done in the conventional and low-voltage mode.

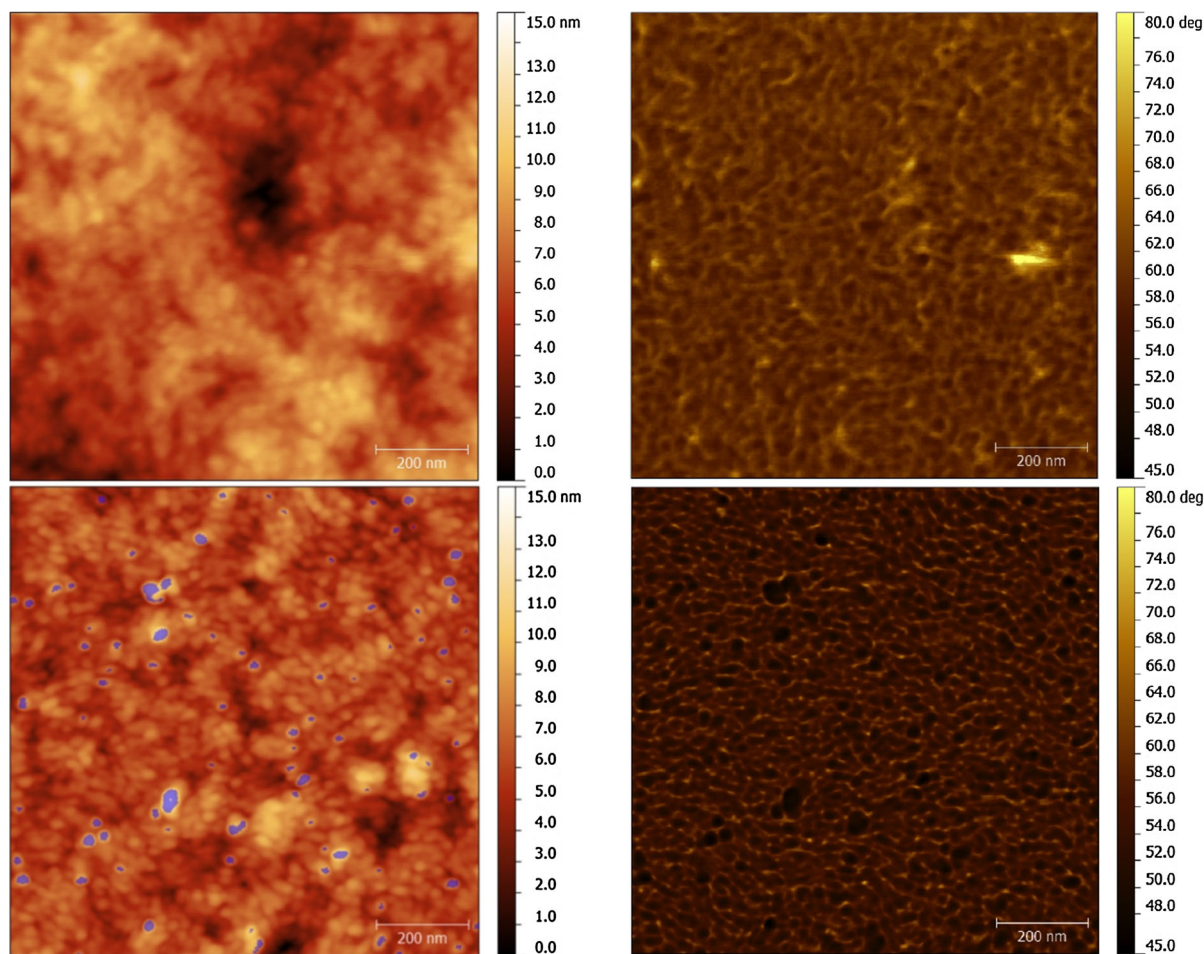
No difference between the surface structure of the fibers with and without additional xylan could be recognized which is in accordance with Köhnke and Gatenholm (2007). Also LVSEM did not visualize any difference between the different surfaces. This could be due to a colloidal size range of precipitated xylan (Linder et al. 2003). This means that the size of the adsorbed/precipitated xylan is small and might look just like the sample. This method is not feasible to detect small xylan aggregates on pulp fibers.

### AFM with OH-functionalized tips

Since xylan could not be visualized on the fiber surface by conventional SEM and LVSEM, AFM was used to detect morphological and topographical differences related to precipitated xylan. Linder et al. (2003) recognized an increase in the quantity and growth in the size of particles on bacterial cellulose by AFM after treatment with a xylan solution. Westbye et al. (2006) discovered a similar surface texture on bleached softwood kraft pulp after the adsorption of different xyans by AFM measurements. In the present study, a new method was applied using OH-functionalized AFM tips were used to scan the surface of thin cellulose model films, derived from trimethylsilyl cellulose, before and after adsorption of xylan. Pretests on pulp fibers resulted in brushing the functional OH groups off the tips, due to the rough surfaces. Since it is a new method, the methodology needs to be further adjusted to scan the surface of fibers with functionalized AFM tips. Therefore, cellulose model films were used, with the knowledge that the chemical composition of such a model film is different to pulp fibers.

The topography and the phase contrast of an amorphous cellulose film before the treatment with the xylan solution are presented in Fig. 2 (top left and right) which looks similar to topography images depicted by Mohan et al. (2012). The surface exhibits large areas of the same height with a homogeneous and uniform phase contrast, meaning the surface of the regenerated cellulose film is relatively smooth. After the treatment with the xylan solution, the cellulose film still appears smooth, but particles of different sizes with diameters between 10 and 15 nm can be detected at irregular distances. These areas are marked in blue in the topography image in Fig. 2 (bottom left). Further, these particles exhibit a lower attraction to the

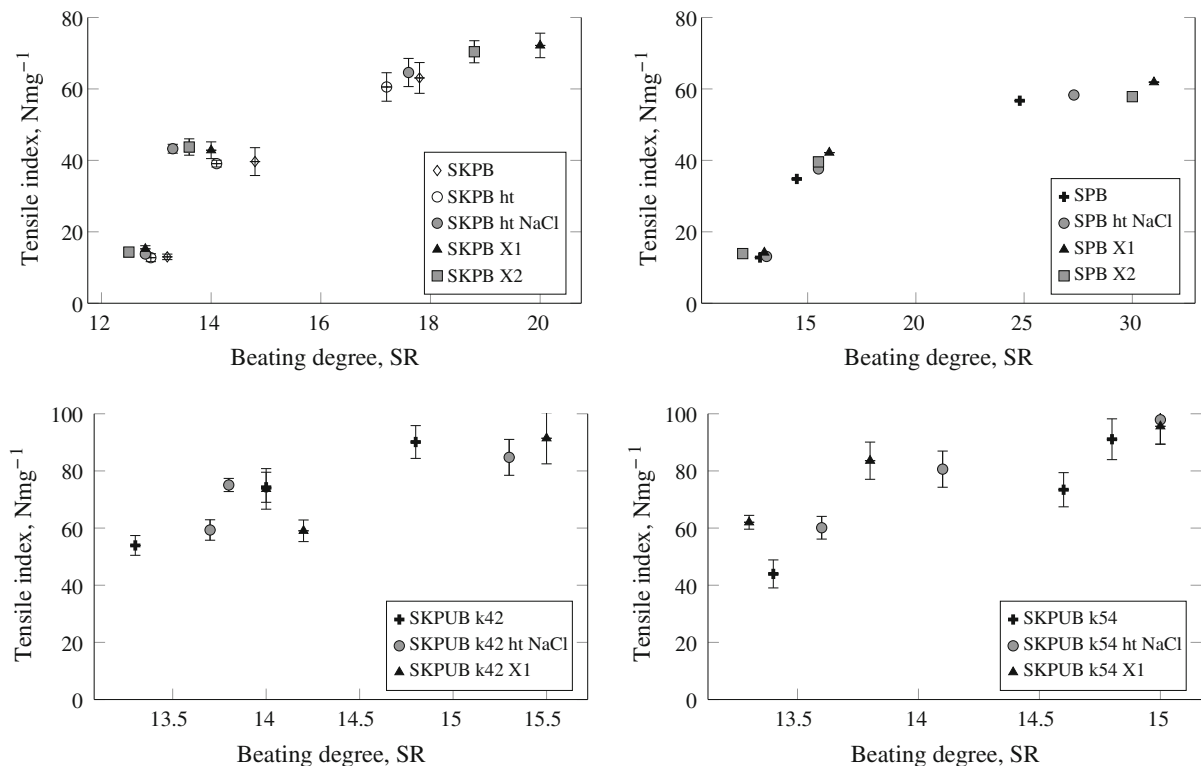




**Fig. 2** Topography (*left*) and phase contrast (*right*) of regenerated cellulose before (*top*) and after the treatment with xylan solution (*bottom*). The images were scanned with an OH-functionalized AFM tip. The *blue areas* (*bottom left*) represent adsorbed xylan

OH groups at the functionalized AFM tip, as depicted as darker areas in the phase contrast image (Fig. 2, bottom right). Besides hydroxyl groups, xylan carries carboxyl groups as well, which feature a higher negative charge density than hydroxyl groups. This implies that a stronger repulsion and lower adhesion between these groups is expected. In fact, lower adhesion forces were determined in the darker areas ( $4.7 \pm 1.3$  nN) than for regenerated cellulose ( $10.2 \pm 2.6$  nN) via force mapping measurements. In force mapping, force-distance ( $F$ - $x$ ) curves are recorded as a function of the lateral coordinates. From these  $F$ - $x$  curves, the adhesion force is extracted. The adhesion force is the force that is needed to separate the tip from the surface after contact (Heinz and Hoh

1999). The findings support the results generated by ATR spectroscopy as well. Therefore, it is suggested that the darker areas in the phase contrast image (Fig. 2, bottom right) are related to precipitated xylan. Recently, measurements were done with the AFM on pulp fibers and also in this case a non-uniform distribution of xylan was obtained. These results will be published together with a detailed description of the method elsewhere. Nevertheless, further questions have to be answered, like the stability of such functionalized AFM tips. However, with this technique it is possible to investigate not only the distribution of xylan on cellulosic surfaces, but also to study the adhesion forces of cellulose and xylan on various substrates.



**Fig. 3** Trend of the tensile index versus the beating degree of: *top right* xylan-modified and unmodified bleached softwood kraft handsheets; *top left* xylan-modified and unmodified bleached sulfite handsheets; *bottom right* xylan-modified and

unmodified unbleached softwood kraft handsheets ( $\kappa 42$ ); and *bottom left* xylan-modified and unmodified unbleached softwood kraft handsheets ( $\kappa 54$ )

### Strength properties

Handsheets were made of the refined and unrefined pulp samples. At the same refining intensity (revolutions with the PFI mill), the xylan-treated samples had a higher tensile index and lower tear index as the reference samples which is in consistence with Dahlman et al. (2003), Köhnke et al. (2008), and Silva et al. (2011). However, the beating degree was more affected for the modified pulp samples. This means that the physical properties of the pulps changed more significantly. Comparing again the tensile index versus the beating degree, the effect of additional xylan on the physical strength properties is negligible which is in agreement with Köhnke and Gatenholm (2007). This is illustrated in Fig. 3. A similar trend was observed for the tear index, stretch at break, or sheet density. No effect of xylan on the strength properties of the VFs could be recognized which is not surprising, since no adsorption/

precipitation of xylan onto the VFs could be observed by HPLC.

The reason for this behavior may be the nonuniform distribution and the amount of precipitated xylan on the fiber surface. This results in areas with higher and lower amounts of xylan. Therefore, it is dependent on the presence of precipitated xylan in the bond of adjacent fibers. However, an area-wide attachment of xylan on the fiber surface might have a larger impact on the strength properties of paper. Xylan also exhibits glucuronic acid groups which can develop more as well as stronger bonds between adjacent fibers via coulomb forces. Nevertheless, xylan features a much lower degree of substitution, molecular weight, and degree of polymerization than common additives, e.g. carboxymethyl cellulose. However, xylan and other hemicelluloses do have an impact on the strength properties, which are in general lower after extraction, although a direct correlation is not always reported in the literature (Leopold and McIntosh 1961; McIntosh

1963; Pettersson and Rydholm 1961; Ratcliff 1949; Spiegelberg 1966).

When comparing additional xylan on fibers with other polysaccharides, e.g. xyloglucan or carboxymethyl cellulose (CMC), similar trends can be found. Christiernin et al. (2003) concluded, that additional xyloglucan increased the strength slightly due to stronger bonds and /or better formation of the paper, but the WRV was also increased. The addition of CMC also affects the strength properties of paper (Alén 2007). This is explained by a higher surface charge and the formation of additional bonds between adjacent fibers. However, a higher negative surface charge results in a stronger swelling behavior of the fibers and consequently a higher effort is need for paper drying (Weber et al. 2013). Cationic polysaccharides, e.g. cationized starch or xylan adsorb more strongly on the slightly negative surface of cellulose fibers and introduce positive charges which increase the number of coulomb forces between adjacent fibers (Alén 2007; Ren et al. 2009; Schwikal et al. 2011). The swelling behavior was found to be not significantly affected by positive charges (Weber et al. 2013).

Moreover, pulp fibers already hold xylan as well as other hemicelluloses (e.g. mannan) on the surface and within the fiber cell wall. Thus, it could be possible that the morphology and the chemical composition of both, the fiber surface and the cell wall, determine the strength properties of a paper network even more than additional xylan by adsorption/precipitation.

## Conclusions and outlook

The precipitation of xylan on the pulp samples resulted in an increased content of xylan. The amount of additional xylan was in the order of bleached softwood kraft pulp (SKPB) > unbleached softwood kraft pulp (SKPUB) > bleached sulfite pulp (SPB). No adsorption/precipitation of xylan was detectable onto the viscose fibers (VFs).

A stronger increase in the beating degree of the pulp samples treated with xylan occurred after refining. However, comparing strength properties of the handsheets versus the beating degree, no difference between the reference samples and the modified pulps could be recognized. With regard to the refining intensity (revolutions in the PFI mill), the handsheets of the modified pulps feature higher tensile strength.

The surface analysis by ATR of the SKPB fibers after the treatment with xylan observed a heterogenous distribution on the surface. With the help of SEM in the conventional and low-voltage mode, adsorbed/precipitated xylan could not be visualized. The analysis of the distribution of xylan on cellulose model films by AFM with functionalized tips also observed a nonuniformly arrangement on the surface. Xylan was distributed as particles with a diameter of 10–15 nm on the model films. During force mapping the particles featured a lower adhesive force (5–10 nN), than the pure cellulose. The present limitation is the surface roughness of pulp fibers. On rough surfaces, the functional groups are easily brushed off during scanning.

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