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Modification of pine pulp during oxygen delignification by xylan self-assembly

Olga Grigoray[a], Joakim Järnström[a], Elina Heikkilä[a], Pedro Fardim[a,*], Thomas Heinze[a,b]

[a] Laboratory of Fiber and Cellulose Technology, Åbo Akademi University, Porthansgatan 3, FI-20500, Åbo, Finland
[b] Center of Excellence for Polysaccharide Research, Institute of Organic Chemistry and Macromolecular Chemistry, Friedrich Schiller University of Jena, Humboldtstraße 10, 07743 Jena, Germany

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ABSTRACT

Self-assembly is a technique of preparing functional materials based on targeted intermolecular interactions involving different macromolecules. In this work, hardwood xylan was disassembled from wood and birch bleached kraft pulp using pressurized hot water extraction (HWX) and cold alkali extraction (CAX), respectively. The extracted biopolymers were characterized using gas chromatography (GC), size exclusion chromatography (SEC) and Fourier transform infrared spectroscopy (FTIR), and subsequently added into an oxygen delignification reactor containing pine kraft pulp. The assembly of xylan-pulp fiber was characterized using advanced time-of-flight secondary ion mass spectrometry (ToF-SIMS) and imaging. The xylan-pine pulp assembly was not significantly removed during the whole elemental chlorine free bleaching sequence or during low consistency refining. Modified fibers had superior mechanical properties compared to the reference pulp. Our concept can be easily applied in the pulp and paper industry, and it opens new possibilities for the utilization of fully bio-based fibers in new materials.

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1. Introduction

The natural composition of wood pulp fibers, isolated by a chemical or mechanical pulping process, offers a platform for ubiquitous biomaterial applications such as paper, board and composites. Wood and non-wood plant cells primarily consist of three polymeric components: lignin, cellulose and hemicelluloses. These biopolymers are organized into an ingenious nature-engineered structure, forming a durable material with unique properties, set by the specific demands of the species, the place of growth, and part of the plant where the cell is formed. Each component makes its own contribution to the material properties viz., cellulose provides reinforcement, lignin gives stiffness (Zhang et al., 2013) and hemicelluloses bind these two together and offer elasticity to the structure (Spiegelberg, 1966).

Hemicelluloses are cell wall heteropolysaccharides of lower molar mass than cellulose (Sixta, 2006). They can be isolated from the plant by hot water or alkali extraction. Xylans are the most common hemicelluloses and considered to be the second most common biopolymer in the plant kingdom. Xylans derived from wood consist of a backbone of anhydroxylose units linked by β-(1 → 4)-glycosidic bonds with different attached substituents, e.g. 4-*O*-methylglucuronic acid, arabinofuranose or acetyl groups (Fengel & Wegener, 1984). In the cell wall, it is believed that they are mainly associated with lignin (Salmen & Olsson, 1998).

During chemical pulping, the composition of fibers is severely altered, and about half of the wood weight is dissolved in the kraft pulping liquor (van Heiningen, 2006). Spent cooking solution (black liquor) containing lignin, carbohydrates and products of their degradation, is combusted to produce steam and electricity, and to recover pulping chemicals. Combustion of lignin is reasonable because it has a relatively high calorific value (25 MJ/kg) compared to that of carbohydrates (14 MJ/kg) (Janzon, Saake, & Puls, 2008). However, hemicelluloses like xylan could be further utilized as functional biopolymers, adding significant value to the end product in different applications. Due to its end group configuration and substituents, xylan is a relatively stable hemicellulose (Johansson & Samuelson, 1977). Further, the globally increasing need for raw materials as well as the increasingly specified environmental aspects generates interest in better use of the valuable biopolymer resources.

* Corresponding author at: Åbo Akademi University, Laboratory of Fiber and Cellulose Technology, Porthansgatan 3, FI-20500 Turku/Åbo, Finland.
Tel.: +358 504096424.
E-mail address: pfardim@abo.fi (P. Fardim).

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Modification of pulp fibers is one of the possible xylan applications. As it was shown previously (Silva et al., 2011; Köhnke, Pujolras, Roubroeks, & Gatenholm, 2008; Muguet, Pedrazzi, & Colodette, 2011), adsorption of xylan has a positive impact on the pulp beatability, which means, the ability of fibers to become more flexible and more fibrillated during mechanical treatment at lower energy consumption. The addition of xylan also enhances the strength properties of fiber networks (Schönberg, Oksanen, Suurnäkki, Kettunen, & Buchert, 2001; Muguet et al., 2011). Tensile and tear strength correlate well with the cellulose/hemicellulose ratio, the first one having a negative correlation and the other a positive correlation with the ratio (Danielsson, 2007).

Mechanism of xylan adsorption onto pulp fibers has been studied previously by several research groups (Henriksson & Gatenholm, 2001; Linder, Bergman, Bodin, & Gatenholm, 2003; Westbye, Svanberg, & Gatenholm, 2006). It was found that, the main driving force for adsorption is the formation of hydrogen bonds between xylan and the cellulose fibers. Also, it was suggested that xylan adsorbs on the fibers in the form of aggregates. In aqueous solution, xylan chains interact via hydrogen bonds and hydrophobic interactions forming associated structures. At high temperature and alkaline conditions, xylan loses some of the glucuronic acid and acetyl groups. Split of glucuronic acid groups results in a decrease of the repulsion between the xylan chains, and deacetylation leads to a lower solubility of xylan. Both these phenomena facilitate aggregation and assembly of xylan on the fiber surfaces.

The extra xylan has been normally added during the cooking process (Danielsson, 2007), or after bleaching (Schönberg et al., 2001; Silva et al., 2011). Muguet et al. (2011) have recently shown that xylan can be successfully added during the oxygen delignification stage of eucalyptus, before the primary bleaching sequence. However, there is no previous knowledge about the impact of the xylan sorption on the fiber surface chemistry and sorption of hardwood xylan onto softwood fibers under oxygen delignification conditions.

The aim of this work was to investigate the modification of pine kraft pulp fibers by directed self-assembly of hardwood xylan, where the fiber properties can be tuned in a fully bio-based concept. Two different types of xylans, extracted from birch wood and bleached kraft pulp, were used to modify the fibers. The study on the mechanism of xylan assembly during oxygen delignification and effects on fiber topochemistry were of interest. Moreover, the tolerance of xylan-fiber assembly during whole bleaching and refining of the modified fibers was investigated.

2. Experimental part

2.1. Materials

Unbleached pine kraft pulp and bleached birch kraft pulp were obtained from Metsä Fiber Oy Rauma Mill (Finland). The unbleached pulp was washed and screened with a Valmet TAP 3.3 screen (0.15 mm slots). Birch chips were collected from UPM mill (Lappeenranta, Finland) and screened to fractions 2–8 mm.

2.2. Methods

2.2.1. Isolation of the xylans

Hot water extracted xylan (HWX) was isolated from the screened birch chips using a cylindrical rocking digester. The extraction was carried out with the wood-to-water ratio 1:5, at 160 °C for 10 min and a heating rate of 2 °C/min. After the extraction the liquor was concentrated by evaporation under vacuum at 42 °C. The xylan was precipitated over night with ethanol in the ratio of 1:8. The precipitated xylan was filtered off, washed with ethanol, and freeze-dried. (Vega, Petzold-Welcke, Fardim, & Heinze, 2012)

The cold alkali extracted xylan (CAX) was isolated from bleached birch kraft pulp. The xylan was extracted for 30 min at room temperature with 1 M NaOH solution. The pulp consistency was 10%. Xylan was precipitated from the solution by neutralizing with 1 M hydrochloric acid. The precipitated xylan was filtered off, washed with ethanol and water, and freeze-dried. (Sixta, 2006)

2.2.2. Analysis of the extracted xylans

2.2.2.1. Gas chromatography (GC). The compositions of the extracted xylans were studied by acid methanolysis and GC as described elsewhere (Sundberg, Sundberg, Lillandt, & Holmbom, 1996) with minor adjustments. The samples were left to react with the methanolysis reagents for 3 hours at 105 °C. The samples were neutralized with 200 μl of pyridine, and 1 ml of resorcinol (0.1 mg/ml) dissolved in methanol was added as internal standard. The operating conditions of the GC were as follows: column J&W HP-1, 25 m × 0.200 mm (ID), film thickness 0.11 μm; the injector temperature 250 °C, the split ratio 1:25; the temperature program of the oven 100 °C, 1 min, 4 °C/min, 170 °C, 12 °C/min, 300 °C, 7 min. The temperature of the flame ionization detector (FID) was 310 °C.

2.2.2.2. Fourier transform infrared—Attenuated total reflectance spectroscopy (FTIR-ATR). The FTIR-ATR spectra were measured with Nicolet iS50 FT-IR spectrometer. The samples were pressed against a diamond crystal and the spectra were recorded in the range of 500–4000 cm^{-1} with the resolution 4 cm^{-1} and the number of scans performed was 32.

2.2.2.3. Pyrolysis-gas chromatography–mass spectrometry (Py-GC–MS). Py-GC–MS analysis was used as a qualitative method for lignin determination. Py-GC–MS analysis was done with a filament pulse resistance-heated pyrolyser Pyrola 2000 (Pyrol AB, Lund, Sweden) connected to an HP 6890-5973 GC-quadrupole-MSD instrument (Hewlett-Packard, Palo Alto, CA). The samples were pyrolyzed at 600 °C for 2 s, at a chamber temperature of 175 °C. The GC column used was 25 m × 0.2 mm × 0.11 μm HP-5 (Agilent Technologies Inc., Santa Clara, CA), and helium was used as the carrier gas at a flow rate of 0.8 ml/min. The oven temperature was programmed from 50 °C (held for 0.5 min) to 300 °C at 8 °C/min. The injector temperature was 260 °C with a split at 20 ml/min. The ionization mode was electron ionization at 70 eV. The pyrolysis compounds were identified by comparing the spectra with Wiley 275 and NIST 98 and laboratory's own mass spectral libraries.

2.2.2.4. Size exclusion chromatography (SEC). The molecular weight of the xylans was evaluated by SEC using a system from JASCO (Tokyo, Japan), including a SEC-pump PU-980, RI detector (RI-930) and NOVEMA 3000 and 300 columns. The samples were dissolved in DMSO solution of LiBr (1 g/l). The injection volume was 100 μl, a flow rate was 0.5 ml/min and the temperature was 65 °C. The results were computed using software WinGPC (Polymer standard service, PSS Mainz, Germany). Pullulan was used as a standard.

2.2.2.5. Lignin determination. Lignin content was determined according to TAPPI T 222 om-02 for acid-insoluble and TAPPI UM 250 for acid-soluble lignin.

2.2.3. Modification of the pulp fibers, bleaching and beating

HWX and CAX were introduced for modification of pine kraft pulp during oxygen delignification stage. The delignification was carried out in a Quantum Mark IV (Akron, United States) reactor. The dry xylans dispersed in water were added to the reactor simultaneously with NaOH solution. The pH was adjusted to 11 (Eriksson, Samuelson, & Viale, 1963). Two different xylan dosages

Table 1
Conditions for oxygen delignification and bleaching sequence.

Parameters	O[a]	D_0[a]	EOP[a]	D_1[a]
Consistency [%]	10	6	8	8
Temp. [°C]	95	60	80	75
pH	11	2–2.5	11	4.5–5
Reaction time [min]	60	60	80	200
O_2 pressure [bar]	6		2.8	
NaOH [g/kg]	20		20	
ClO_2 [g/kg]		5		8
H_2O_2 [g/kg]			6	

[a] Oxygen delignification stage (O), chlorine dioxide bleaching stage (D_0 and D_1) and hydrogen peroxide reinforced alkaline extraction stage (EOP).

were applied: 2% and 5% (w/w based on dry pulp). The conditions of the oxygen delignification are specified in Table 1. After the oxygen delignification stage, the pulp was bleached in a short bleaching sequence, D_0-EOP-D_1. The chlorine dioxide bleaching stages (D_0, D_1) were performed in plastic bags placed into a thermostatic water bath. The oxygen and hydrogen peroxide reinforced alkaline extraction stage (EOP) was done in the same reactor as the oxygen delignification stage. Conditions of the bleaching stages are shown in Table 1 (Gullichsen, 2000). After each bleaching stage the pulps were washed until clear filtrates and neutral pH were obtained.

After the bleaching, the pulps were beaten in a valley beater according to ISO 5264/1-1979. Water samples were taken from the beating water to evaluate desorption of xylan during beating. The Schopper-Riegler number (SR, ISO 5267/1-1979) for the beaten pulps was between 30 and 33.

2.2.4. Analysis of the pulp samples

2.2.4.1. Standard methods. To evaluate pulp properties the following standard methods were used: kappa number (ISO 302-1981), hexenuronic acid groups (HexA) content (Chai, Zhu, & Li, 2001), intrinsic viscosity (ISO 5351/1-1981), brightness (ISO 2470-1977), and water retention value (WRV, SCAN-C 62:00). The hand-sheets were prepared according to SCAN-CM 11:95. Air permeability, tensile index and tear index of the hand-sheets were measured using ISO 5636/1-1984, ISO 1924-2:1992 and ISO 1974:1990, respectively.

2.2.4.2. High performance anion exchange chromatography with pulsed amperometric detection (HPAE-PAD). The amount of xylan adsorbed onto the fibers as well as desorbed during the beating was evaluated by HPAE-PAD with Dionex ICS 5000 (Sunnyvale, United states) system and capillary PA20 CarboPac anion-exchange resin column (0.4 × 150 mm) operated at 30 °C. Potassium hydroxide was used as an eluent at a flow rate of 0.008 ml/min. The concentration gradient of the eluent was the following: 0–12 min with 1 mM KOH, 12–17 min with 5 mM KOH and 17–21 min with 10 mM KOH. An injected volume of the samples was 20 μl. Before the injection, the samples were hydrolyzed with 72% sulphuric acid (Sundberg, Pranovich, & Holmbom, 2003) and then neutralized with barium hydroxide. Sorbitol was used as an internal standard. The calibration was performed with standard solutions of arabinose, glucose, xylose, mannose, rahmnose, and galactose prepared with different concentrations in deionized water.

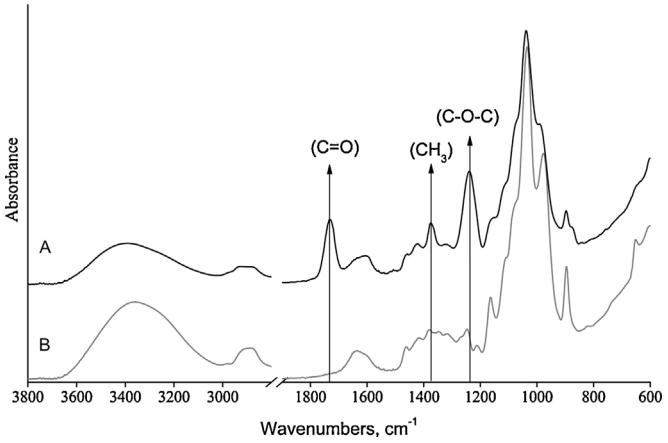

Fig. 1. FTIR-ATR spectra for hot water extracted (A) and cold alkali extracted (B) xylans.

2.2.4.3. Time-of-flight secondary ion mass spectrometry (ToF-SIMS). Air-dried pulp samples were analyzed using an Electronics ToF-SIMS TRIFT II spectrometer with a $^{69}Ga^+$ primary ion beam. The raster size was 200 μm × 200 μm with a resolution of 256 × 256 pixels. The spectrometer was operated in the positive mode with 25 kV applied voltage and 600 pA aperture current.

3. Results and discussions

3.1. Xylan characterization

Sugar composition of the extracted xylans was analyzed by acid methanolysis and GC. As expected, the predominant sugar in the structure of the hemicelluloses was xylose (Table 2). CAX and HWX contained 79.4% and 51.0% of anhydroxylose units. Besides xylose, native xylan carries 4-*O*-methylglucuronic acid groups and *O*-acetyl groups linked to the xylose backbone as the side groups. The amount of the glucuronic acid groups in CAX (1.6%) was lower than that in HWX (3.4%) due to the cleavage of the glycosidic bonds between the glucuronic acid groups and xylan backbone, and a partial conversion of these groups to hexenuronic acid groups during the kraft cooking (Sixta, 2006). The following bleaching also decreases the amount of glucuronic acid groups (Muguet et al., 2011). Mannose, glucose, galactose, rhamnose and galacturonic acid, which are attributed to other hemicelluloses and pectins, were present in a significantly lower amount, especially in the case of CAX.

In native xylan, amount of acetyl groups corresponds to a molar ratio of 1:0.5 to 1:0.6 (xylose: acetyl) (Fengel & Wegener, 1984). However, pressurized hot water extraction causes releasing some part of acetyl groups as acetic acid. The xylan extracted from the kraft pulp lost the acetyl groups in cooking process due to deacetylation in the alkaline media. It is supported by the study of the extracted xylans with FTIR. FTIR-ATR spectrum of HWX (Fig. 1) showed bands originating from acetyl groups: 1732 cm^{-1}, 1375 cm^{-1} and 1239 cm^{-1} that were assigned to C=O symmetrical stretching vibration, C—H symmetrical deformation

Table 2
Carbohydrate composition of hot water extracted (HWX) and cold alkali extracted (CAX) xylans by acid methanolysis and gas chromatography.

Sample	Carbohydrates, % (g/g)								
	Ara[a]	Xyl[a]	Rha[a]	Man[a]	Glc[a]	Gal[a]	GlcA[a]	Me-GlcA[a]	GalA[a]
HWX	0.12	51.01	0.88	4.38	3.12	3.04	0.16	3.41	1.42
CAX	0.12	79.35	0.08	0.03	0.02	0.04	0.00	1.55	0.00

[a] Arabinose (Ara), xylose (Xyl), rhamnose (Rha), mannose (Man), glucose (Glc), galactose (Gal), GlcA (glucuronic acid), 4-*O*-methylglucuronic acid (Me-GlcA) and galacturonic acid (GalA).

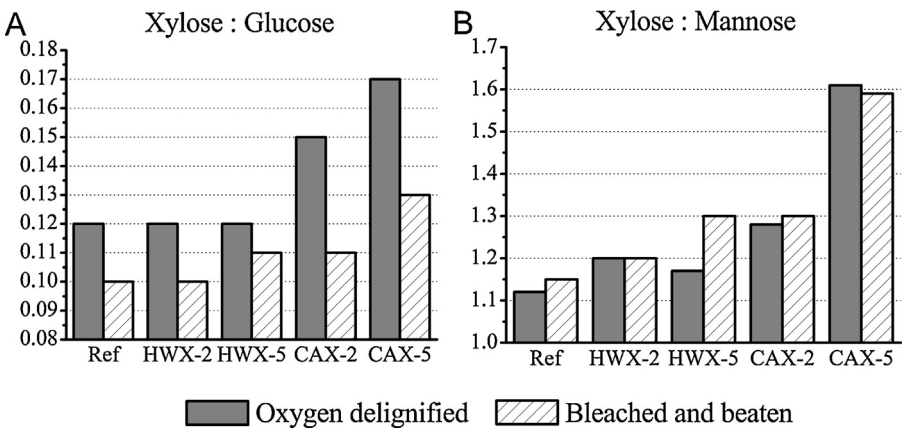

Fig. 2. Ratio of xylose to glucose (A) and xylose to mannose (B) in pulps after oxygen delignification, and bleaching and beating. Error margins are within 5%. HWX and CAX pulps modified during oxygen delignification by 2 and 5% (w/w) of hot water extracted xylan and cold alkali extracted xylan, respectively.

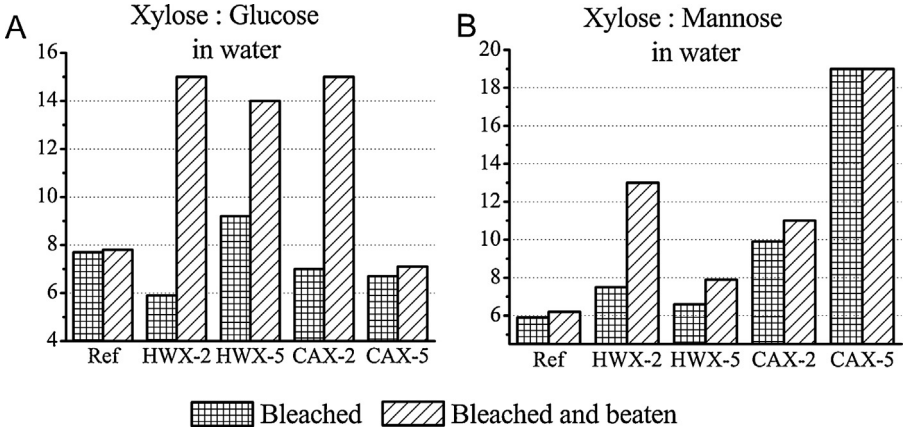

Fig. 3. Ratio of xylose to glucose (A) and xylose to mannose (B) in water before and after beating of bleached samples. Error margins are within 5%. HWX and CAX pulps modified during oxygen delignification by 2 and 5% (w/w) of hot water extracted xylan and cold alkali extracted xylan, respectively.

and C—O—C asymmetrical stretching vibration, respectively (Buslov et al., 2009; Yilgor, Dogu, Moore, Terzi, & Kartal, 2013; Mohebby, 2008; Socrates, 2001). On the contrary, the spectrum of CAX did not contain such bands.

Another important difference between HWX and CAX was the presence of impurities in the form of lignin that could be observed as a colour difference, slight brownish and white, respectively. Py-GC–MS was used as a qualitative method for lignin determination. The treatment of data for both xylans revealed that the spectra of HWX contained pyrolysis products of syringyl lignin units in HWX. The analysis of lignin content confirmed that HWX contained 4.8% of lignin. Molar mass distribution studied by SEC showed that HWX consisted of two fractions with weight-average molecular masses (M_w) of 5.0×10^3 g/mol and 6.5×10^7 g/mol. It could be suggested that the second fraction was the aggregates of lignin-carbohydrate complexes. CAX had one fraction with M_w of 2.8×10^4 g/mol.

In summary, CAX had higher purity compared to HWX which is explained by the fact that it was subjected to pulping, bleaching and alkali extraction processes. On the other hand, the isolation of xylan by pressurized hot water extraction preserved the side groups of native xylan to some extent. These findings are in agreement with the results reported earlier (Liu, Fatehi, Sadeghi, & Ni, 2011; Vega et al., 2012; Muguet et al., 2011; Westbye et al., 2006).

3.2. Xylan adsorption

HWX and CAX were applied for modification of the pine kraft pulp fibers during the oxygen delignification stage at dosages of 2 and 5% (w/w, based on dry pulp). The xylan adsorption onto the pulp was evaluated after hydrolyzing the pulps and analyzing the sugar composition by HPAE-PAD. Assembly of added xylans was verified by the increase of xylose-to-glucose and xylose-to-mannose ratios in the oxygen delignified pulps (Fig. 2). CAX was adsorbed at a higher extent than HWX in addition to the higher content of xylose in the structure. This could be explained by the difference

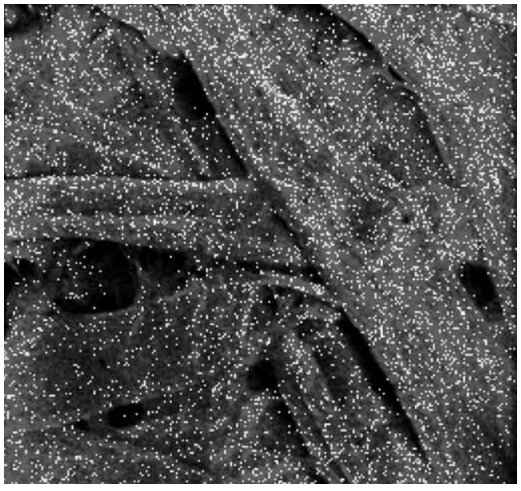

Fig. 4. ToF-SIMS surface map of bleached and beaten sample CAX-5. The xylan (115 Da, $C_5H_7O^{3+}$) is shown in white. CAX pulp modified during oxygen delignification by 5% (w/w) of cold alkali extracted xylan.

in the purity of the xylans. The removal of acetyl groups decreases the solubility of the CAX that facilitates its deposition onto the fiber surfaces. The lower amount of glucuronic acid side groups reduces repulsion between CAX chains and, therefore, induces its aggregation and adsorption on the fiber. Also, reduced negative charge of the xylan causes less repulsion between the polymer and the fibers resulting in a better interaction. In addition, a molecule with high molecular mass loses less entropy on the adsorption and has more sites available for the interaction (Köhnke, 2010). A similar effect of purity on xylan deposition during oxygen delignification stage was reported by Muguet et al. (2011).

3.3. Xylan resistance to pulp processing

After the whole bleaching sequence and beating, the xylose-to-glucose ratio was lower compared to the ratio after the oxygen delignification for the corresponding pulps, indicating the desorption of xylan during the bleaching and beating process (Fig. 2). However, a part of the assembled xylan stayed on the pulp fibers during processing, which was inferred by comparing the reference sample with the pulps treated with xylans.

The amount of dissolved material in the beating water was very low (<0.01%, w/w). The beating seemed to increase the relative amount of xylose in the beating water for the pulps with added xylan (Fig. 3). However, in case of CAX5, the sample containing the largest amount of added xylan, practically no difference was found between the water samples before and after beating.

3.4. Surface characterization of modified fibers

In the ToF-SIMS analysis, the characteristic peaks of xylan, that is, pentose monomer fragments $C_5H_7O_3^+$ (*m/z* 115) and $C_5H_9O_4^+$ (*m/z* 133), and cellulose, that is, hexose monomer fragments $C_6H_7O_3^+$ (*m/z* 127) and $C_6H_9O_4^+$ (*m/z* 145), were of main interest (Fardim & Duran, 2003). The relative peak intensities were investigated, listing the relations between the total pentose peak counts and the total hexose peak counts (Table 3). Polysaccharides other

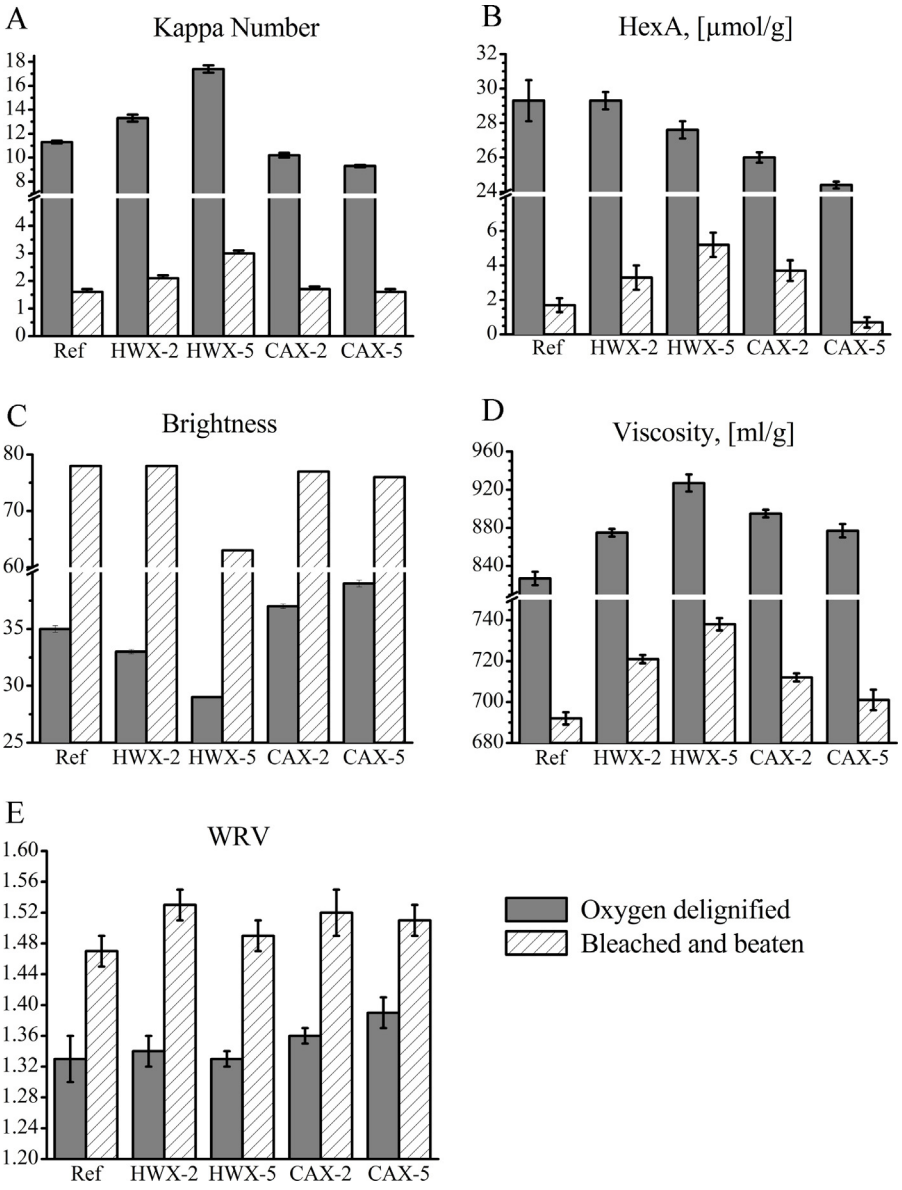

Fig. 5. Pulp properties of the modified fibers. HWX and CAX pulps modified during oxygen delignification by 2 and 5% (w/w) of hot water extracted xylan and cold alkali extracted xylan, respectively.

Table 3
Relative counts of pentose-to-hexose monomers of bleached samples in ToF-SIMS spectra.

Bleached pulp samples	Before beating pentose/hexose	After beating pentose/hexose
Reference	0.90 ± 0.04	0.85 ± 0.01
HWX-2[a]	1.02 ± 0.16	0.89 ± 0.12
HWX-5[a]	1.04 ± 0.05	1.07 ± 0.10
CAX-2[b]	1.18 ± 0.11	1.07 ± 0.07
CAX-5[b]	1.19 ± 0.04	1.27 ± 0.01

[a,b] HWX and CAX pulps modified during oxygen delignification by 2 and 5% (w/w) of hot water extracted xylan and cold alkali extracted xylan, respectively.

than xylan and cellulose can contribute to the occurrence of these mass fragments; however, xylan and cellulose were expected to be the main sources of the peak counts in question. The relative count number of pentose monomers compared to the count number of hexose monomers supported the finding made with HPAE-PAD. This indicated the presence of xylan-pine fiber assembly on the pulp surfaces when xylan was added in the oxygen delignification stage. The pure CAX resulted in the higher pentose-to-hexose ratios than those of HWX. However, there was no difference between 2% and 5% xylan dosage in both cases. It is possible that the increase in the dosage, from 2% to 5%, mainly contributed to xylan assembly deeper in the pores of the fiber wall (Köhnke, Lund, Brelid, & Westman, 2010; Liu et al., 2011).

A part of the surface xylan seemed to be dissolved or desorbed during the beating of the reference and pulps with less added xylan dosages. This finding is in line with the detected monomers in the beating water (Fig. 3). However, in case of pulps with the highest added xylan dosages, the pentose-to-hexose ratio increased after the beating based on ToF-SIMS count numbers. Using ToF-SIMS for quantitative speculations is rather suggestive, but an idea can be proposed that beating had redistributed xylan from the bulk to the outer fiber surfaces. In any case, the xylan-fiber assembly seemed to tolerate beating relatively well.

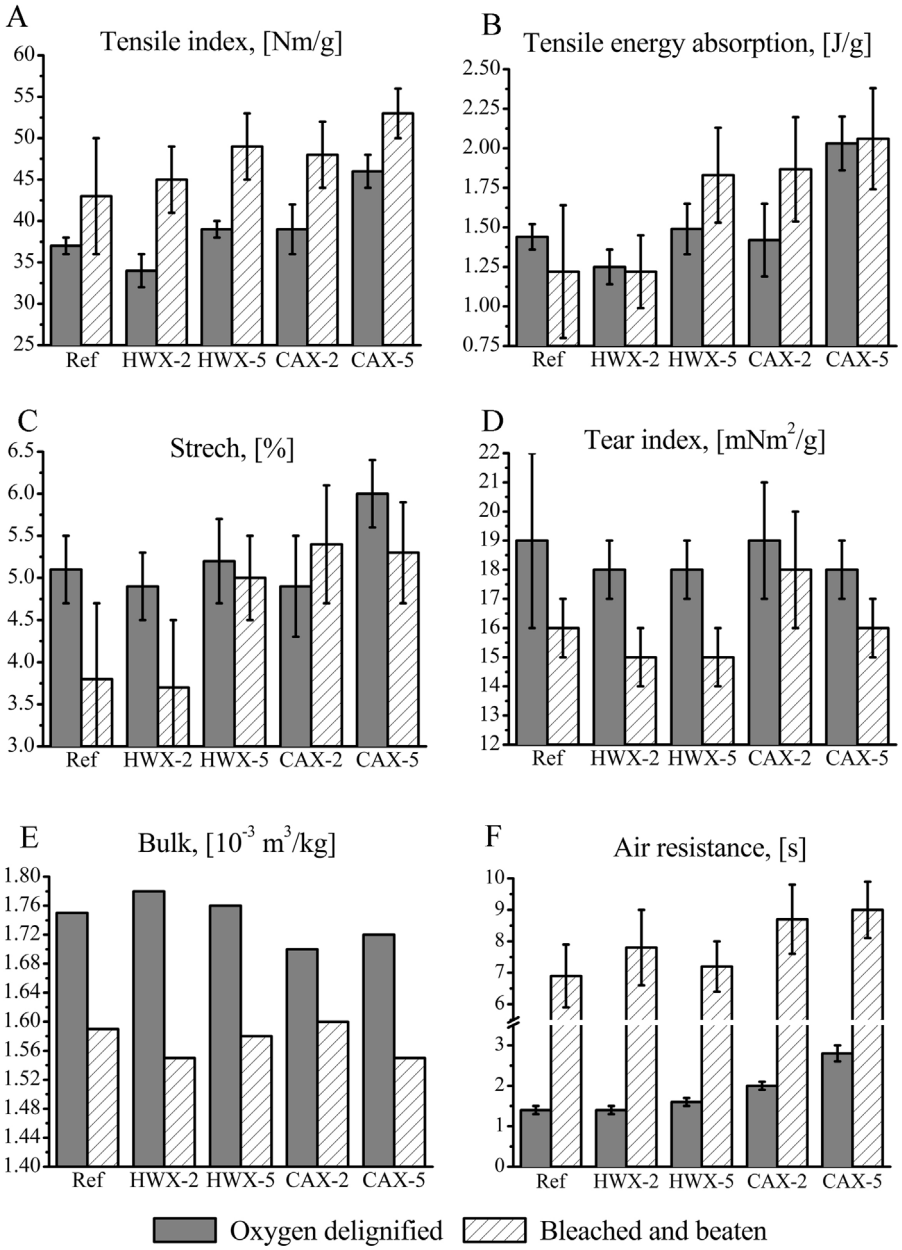

Fig. 6. Hand-sheets properties made of modified fibers. HWX and CAX pulps modified during oxygen delignification by 2 and 5% (w/w) of hot water extracted xylan and cold alkali extracted xylan, respectively.

The distribution of xylan on pulp surfaces was investigated using ToF-SIMS imaging. The occurrence of the mass peaks of pentoses was mapped, and the distribution was found to be uniform over the pulp surface in the investigated scale (Fig. 4). Bleaching did not affect the distribution, and an even surface coverage by xylan assembly was detected still after beating.

3.5. Pulp and sheet properties of the modified fibers

The properties of the modified fibers were compared with those of the reference pulp (Fig. 5). Lignin impurity of HWX resulted in a higher kappa number in the HWX treated samples compared to the reference in both cases after the oxygen delignification and bleaching (Fig. 5A). The difference between the hexenuronic acid content in the reference and HWX treated pulps after the oxygen delignification stage was minimum (Fig. 5B). Hence, the increment in the kappa number was due to the presence of lignin in the xylan. Contribution of HexA to the kappa number was 2–2.5 units for the oxygen delignified samples, since 11.6 μmol/g of hexenuronic acid corresponds to one kappa number unit (Sixta, 2006). After bleaching, amount of hexenuronic acid decreased significantly for each sample. Surprisingly, an addition of pure xylan improved the performance of the oxygen delignification that resulted in a lower kappa number in comparison with the other samples. However, the values for the reference and CAX treated pulps levelled out after the final bleaching stage. The brightness (Fig. 5C) correlated well with the kappa number and decreased with the addition of HWX containing chromophoric compound (lignin).

The viscosity measurement studies explained that there was no direct correlation between the viscosity values and the added xylan (Fig. 5D). As expected, the viscosity values of the bleached and beaten pulps were lower than that of the oxygen delignified pulps due to partial degradation of cellulose. The intrinsic viscosity was primarily affected by the polymers with long chain length. The addition of low molecular weight compounds like xylan could decrease the viscosity of pulp as it was previously shown by Muguet et al. (2011). In comparison with the cited reference, we have employed considerably lower applied dosages which did not cause any decrease in the viscosity. The higher viscosity value of HWX treated pulps can be explained by the influence of lignin–xylan complex of high molecular weight (SEC results).

A small increase in water retention value (WRV) was observed for the xylan modified samples (Fig. 5E). This was related to the increased amount of hydroxyl groups in the fibers after xylan adsorption that led to the increased amount of bound water. WRV correlates well with the tensile strength of fiber web. A change in the WRV, such as 0.1 (g/g), corresponds to the pronounced changes in the tensile index (Scotch, 2005).

The strength and barrier properties of final bleached and beaten hand-sheets made of modified fibers were compared to one made from the reference pulp (Fig. 6). The results indicated that xylan assembly had several positive effects on the hand-sheets strength properties like increased tensile strength, tensile energy absorption and stretching (Fig. 6A–C). The tear index did not change under the xylan adsorption (Fig. 6D). The bulk, an inverse property of density, was also not affected by the addition of the xylans (Fig. 6E). The ability of paper to stretch and absorb energy before breaking is important in the paper manufacturing and printing process, but also for several end products, e.g., paper bags and packing material. Barrier properties are also important for the packing materials. The results showed an improved air resistance for the pulps treated with xylans (Fig. 6F).

Better strength and barrier properties of the bleached and beaten samples in comparison with the oxygen delignified (Fig. 6) could be explained by the lignin removal and fibrillation. Both factors increased the flexibility and ability of the fiber to swell resulting in the improved interaction between the fibers and a denser fiber network. In addition, formation of fines during the processing also improved the air resistance.

Adsorbed xylan increased the contact between the fibers through available hydrogen bonds and consequently made the fiber matrix stronger and denser. Similar trends of increased strength properties have been reported when adding xylan in the beater for beating of jute (Bhaduri, Ghosh, & Sarkar, 1995) and softwood and hardwood kraft pulp (Ban, Chen, Andrews, & van Heiningen, 2011).

4. Conclusions

In this work the modification of pine fibers by the self-assembly of two types of xylan was performed during the oxygen delignification stage. The applied xylans were extracted from birch wood and bleached kraft pulp. The xylan from wood contained acetyl groups and around 5% of lignin. The xylan from kraft pulp had higher molar mass and purity. The adsorption results showed that both biopolymers were adsorbed and evenly distributed on the fiber surfaces. The adsorbed xylans resisted well to the subsequent bleaching and beating. The modified pulp showed improved mechanical properties. The effect was more pronounced in the case when pure xylan was applied. The xylan extracted from the wood had negative impact on the optical properties of fibers because of lignin impurities. Modification with pure xylan also resulted in better barrier properties even at the lower applied dosage.

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