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Studies on the fibre surfaces modified with xylan polyelectrolytes

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ABSTRACT

Xylan was isolated from birch wood chips by using pressurized hot water extraction (PHWE). The extracted xylan was chemically modified yielding three different xylan derivatives (XDs): xylan sulfate (XS), carboxymethyl xylan (CMX) and xylan-4-[*N*,*N*,*N*-trimethylammonium]butyrate chloride (XTMAB). The structure and molecular weight of XDs was determined by using NMR spectroscopy and size exclusion chromatography (SEC). The potential utilization of xylan polyelectrolytes for modifying fibre surfaces was assessed by sorption experiments using bleached pine Kraft pulp as substrate. Polyelectrolyte titration method was chosen for estimating the amount of sorbed XDs onto the fibres. The cationic xylan derivative XTMAB had a strong interaction with fibres while the anionic derivatives did not show any sorption. X-ray photoelectron spectroscopy (XPS) and time of flight secondary ion mass spectrometry (ToF-SIMS) were selected as advanced surface analyses for studying the amount of surface anionic groups and the surface distribution of the XTMAB. XPS and polyelectrolyte titration results suggested that the XTMAB is sorbed onto the fibre surfaces. ToF-SIMS imaging showed that XTMAB was evenly distributed on fibre surfaces.

1. Introduction

Hemicelluloses comprise 20–30% of wood biomass, being the second most important natural polymer after cellulose. However, the utilization of hemicelluloses and their derivatives in industrial applications is still very limited. Hemicelluloses play a positive role in pulping and papermaking processes (e.g., increasing the yield of the process and also improving mechanical and physical properties of the resulting material). Isolation processes can greatly affect the quality of the extracted hemicelluloses (Ebringerová, Hromádková, & Heinze, 2005) and it is difficult to get a homogeneous material even when the same source and experimental conditions are used. Therefore, it is very difficult to find the optimum extraction conditions without significantly affecting the resulting pulp and paper properties (Linder, Bergman, Bodin, & Gatenholm, 2003; Westbye, Svanberg, & Gatenholm, 2006).

The composition of extracted hemicelluloses is also strongly dependent on the source. Hardwood hemicelluloses are mainly glucuronoxylans (GXs), representing about 15–30% of the total dry-mass. They are composed of β-D-xylopyranosyl units linked by β-(1,4) glycosidic bonds with 4-*O*-methylglucupyranosyluronic acid (4-*O*-Meα-Glc*p*A) and acetyl side groups. In average, one unit of 4-*O*-Me-α-Glc*p*A and 3.5–7 acetyl groups can be found per each 10 xylose units (Evtuguin, Tomás, Silva, & Neto, 2003; Sjöström, 1981). Besides these main structural units, GXs may also contain small amounts of L-rhamnose and galacturonic acid. Due to the observed uronic side groups, the resulting polymer has a negative net charge in aqueous media (Schwikal, Heinze, Saake, Puls, Kaya, & Esker, 2011).

Because of the growing interest in new biomass based products and chemicals as well as the increasing interest in creating functional fibres, the extraction of hemicelluloses prior to pulping is being intensively investigated (Gírio, Fonseca, Carvalheiro, Duarte, Marques, & Łukasik, 2010; Helmerius, von Walter, Rova, Berglund, & Hodge, 2010; Li, Saeed, Jahan, Ni, & van Heiningen, 2010; Liu, 2010).

Pressurized hot water extraction (PHWE) with temperatures above 100 °C, operated in either static (batch) or dynamic (flow-through) mode, has been considered as promising method for

Abbreviations: GX, glucuronoxylan; MB, methylene blue; XDs, xylan derivatives; ToF-SIMS, time of flight secondary ion mass spectrometry; XPS, X-ray photoelectron spectroscopy; XS, xylan sulfate; CMX, carboxymethylxylan; XTMAB, xylan-4-[*N*,*N*,*N*-trimethylammonium]butyrate chloride; SAG, surface anionic groups; AGs, anionic groups.

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recovering of hemicelluloses from wood chips (Borrega, Nieminen, & Sixta, 2011; Lei, Liu, Li, & Sun, 2010; Liu, 2010). PHWE allows the extraction of well-preserved native hemicelluloses without removing high amounts of lignin and without affecting cellulose.

Research on sorption of hemicelluloses during pulping processes already started as early as the 1950s with the work of Yllner and Enström (1956, 1957); (Westbye et al., 2006). The utilization of hemicelluloses in cellulose fibre modification has gained a lot of attention in recent years. It has been proven that xylans interact with cellulose and are irreversibly absorbed onto cellulosic surfaces (Linder et al., 2003). Adsorption of the pre-isolated xylans has been shown to improve pulp properties, such as tensile strength, beatability and resistance to hornification (Köhnke, Brelid, & Westman, 2009). However, it is well known that only a low amount of xylan can be adsorbed in comparison with xylan derivatives (Esker, Becker, Jamin, Beppu, Renneckar, & Glasser, 2002). Despite the use of xylans for cellulose fibre modification, these polymers can be transformed into new polymers with promising properties by chemical modification (Heinze, Liebert, & Koschella, 2006). Xylan derivatives (XDs) with ionic functions (e.g. carboxymethyl xylan, hydroxypropyltrimethylammoniun xylan, xylan sulphate, maleate esters, and xylan propionates and hexanoates) as well as XDs with non-ionic functions (e.g., pyroglutamate, furoate and ibuprofen esters of xylan) have been prepared (Belmokaddem, Pinel, Huber, Petit-Conil, & Perez, 2011; Bigand, Pinel, Perez, Rataboul, Huber, & Petit-Conil, 2011; Daus & Heinze, 2010; Daus, Petzold-Welcke, Kötteritzsch, Baumgaertel, Schubert, & Heinze, 2011; Heinze, Koschella, & Ebringerová, 2004; Heinze, Petzold, & Hornig, 2007; Peng, Ren, & Sun, 2010; Petzold, Schwikal, & Heinze, 2006; Petzold, Schwikal, Günther, & Heinze, 2006; Schwikal & Heinze, 2007; Schwikal, Heinze, Ebringerová, & Petzold, 2006; Simkovic, Gedeon, Uhliarikova, Mendichi, & Kirschnerova, 2011). Recently, amphoteric xylan-type hemicelluloses having carboxymethyl and quaternary ammonium groups were prepared by microwave irradiation (Peng, Ren, Zhong, & Sun, 2012).

The reaction of xylan with sodium monochloroacetate in aqueous sodium hydroxide and appropriate slurry medium yields the anionic carboxymethyl xylan ether (Petzold, Schwikal, & Heinze, 2006; Petzold, Schwikal, Günther, et al., 2006). Otherwise, the conversion of xylan with 2,3-epoxypropyltrimethylammonium chloride results the cationic hydroxypropyltrimethylammoniun xylan ether (Schwikal et al., 2006). The cationic hydroxypropyltrimethylammoniun xylans are described to enhance the tensile modulus of pulp compared to the untreated pulp (Schwikal et al., 2011). The synthesis of xylan sulfate as inorganic anionic xylan halfester was efficiently carried out by reaction of the hemicellulose with sulfur trioxide complexes (Daus et al., 2011; Simkovic, Gedeon, Uhliarikova, Mendichi, & Kirschnerova, 2011).

The synthesis of non-ionic xylan esters were described by efficient conversion of the hemicellulose with furan- and pyroglutamic acid as well as ibuprofen and *N*,*N*′-carbonyldiimidazole as activating agent under homogeneous conditions in dimethyl sulfoxide (Daus & Heinze, 2010; Heinze et al., 2007).

In this work, extracted xylan from birch chips was used for preparing the ionic xylan derivatives (XDs): xylan sulfate (XS), carboxymethyl xylan (CMX), and xylan-4-[*N*,*N*,*N*-trimethylammonium]butyrate chloride (XTMAB). The XDs were characterized regarding structure and solubility. Sorption experiments on bleached pine Kraft pulp were performed using the prepared derivatives and polyelectrolyte titration method was chosen for estimating the amount of sorbed XDs. The lateral distribution of XDs on fibre surfaces was assessed by Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS). According to our knowledge, it is the first time that ToF-SIMS was used for analyzing both the mentioned XTMAB and their distribution on fibre surfaces. The collected data will be useful for further analysis of such compound. The global results from this work will also contribute to a better understanding of the interactions between XDs and cellulosic fibres in the searching for materials from natural resources.

2. Materials and methods

2.1. Material

Sulfur trioxide pyridine complex, sodium monochloroacetate, 3-carboxypropyltrimethyl ammonium chloride, *N*,*N*′-carbonyldiimidazole (CDI), *N*,*N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO) were obtained from Sigma-Aldrich. LiCl were purchased from VWR. 2-Propanol, ethanol, methanol, and acetone were reagent grade chemicals.

2.2. Pressurized hot water extraction (PHWE) of xylan

Birch wood xylan was extracted using a static PHWE mode and industrial birch wood chips collected in a Finnish pulp mill. The non-cellulosic polysaccharides content in the chips was determined in previous studies showing 25.4% of xylose, 2.5% of glucose, 2.0% of galacturonic acid, 1.1% of mannose, 1.1% of galactose, 0.6% of rhamnose, 0.5% of arabinose and 0.5% of glucuronic acid (expressed in w/w%). About 1 kg (based on dry weight) of air-dried screened birch chips with size of 2–8 mm, were extracted using 5 l distilled water in a revolving digestor at 160 °C for 10 min. The resulting liquor (pH of 3.8) was concentrated to 1 l under vacuum (42 mbar) at 42 °C. Then 4 l of ethanol was added to the liquor with vigorous stirring during 20 min for precipitating the hemicelluloses. The mixture was left in refrigerator overnight and then the supernatant was removed by vacuum filtration through a MN 640 w filter paper (Macherey-Nagel GmbH and Co. KG, Düren, Germany). The solid was washed three times with ethanol then dried in oven desiccator at 40 °C and finally freeze-dried yielding 10.5 g of xylan with light brown colour.

2.3. Preparation of xylan derivatives

2.3.1. Xylan sulfate (XS)

Xylan sulfate was prepared according to Daus et al. (2011). Briefly, the sulfur trioxide pyridine complex (3.02 g, 18.9 mmol) dissolved in 12 ml DMF was added to 5.00 g xylan (37.8 mmol) dissolved in 100 ml DMF/LiCl. The mixture was allowed to react 5 h at 100 °C. After cooling, the product was precipitated in 600 ml methanol containing 1.52 g NaOH, washed with aqueous methanol (80%, v/v) until the filtrate had a pH value of 7. Then, the material was washed three times with ethanol. After drying at 40 °C under vacuum, the crude product was dissolved in water and dialysed against water (MWCO 500–1000 D), and freeze-dried. Yield: 2.69 g, light brown colour. Elemental analysis (w/w%): C: 36.24, H: 5.23, S: 3.18. DS 0.16, M_w 16,300 g/mol (0.1 M Na_2HPO_4/NaN_3, pullulan as standard). ^{13}C NMR spectroscopy (D_2O) δ (ppm) = 102.2 (C1), 77.0 (C4), 74.4 (C3), 73.3 (C2), 63.6 (C5).

2.3.2. Carboxymethyl xylan (CMX)

Carboxymethyl xylan was prepared according to Petzold, Schwikal, & Heinze (2006). Briefly, xylan (5.00 g, 37.8 mmol) was suspended in 150 ml 2-propanol. After addition of 10 ml aqueous NaOH (15%, w/v), the mixture was allowed to react for 1 h under stirring at room temperature. Sodium monochloroacetate (2.20 g, 18.9 mmol) was added and the mixture was allowed to react 5 h at 55 °C. The polymer was suspended in aqueous methanol (80%, v/v). The suspension was neutralized with diluted acetic acid and washed five times with 100 ml ethanol. Yield: 4.85 g, light brown colour solid, DS 0.50, M_w 16,200 g/mol (0.1 M Na_2HPO_4/NaN_3, pullulan as standard). ^{13}C NMR spectroscopy (D_2O) δ (ppm) = 178.5

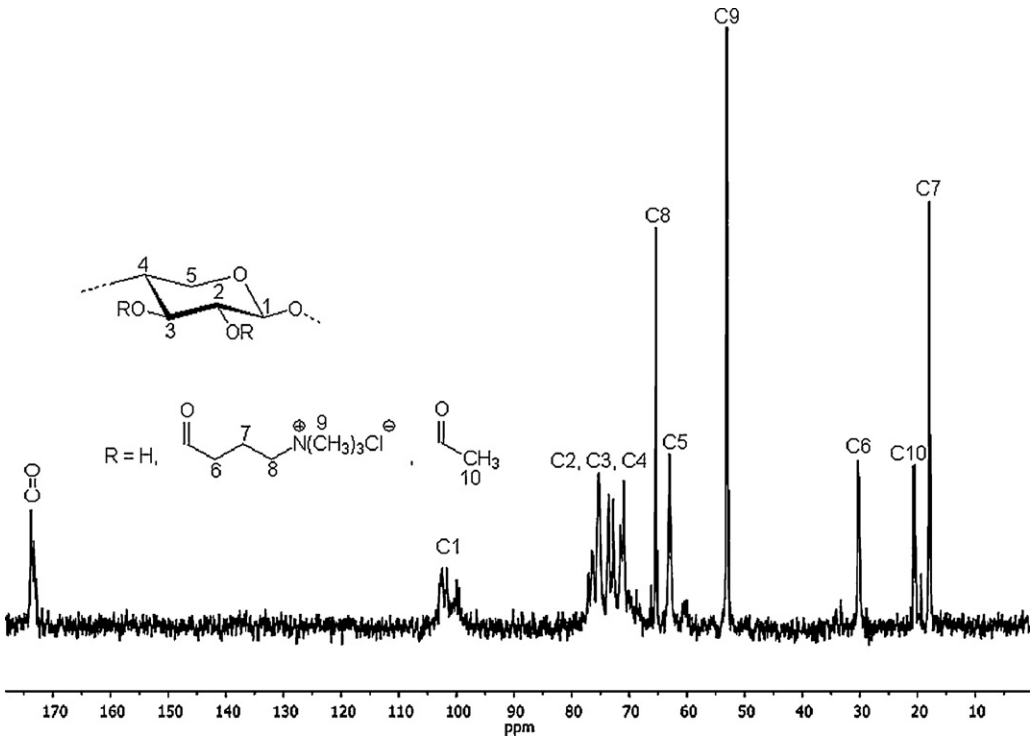


Fig. 1. ^{13}C NMR spectrum of xylan-4-[*N*,*N*,*N*-trimethylammonium]butyrate chloride (XTMAB) in D_2O.

(C=O), 101.3 (C1), 99,7 (C1′), 83.4–80.0 (C3s, C2s), 76.5–71.1 (C4, C3, C2), 70.9 (CH_2COONa), 63.1 (C5).

2.3.3. Xylan-4-[N,N,N-trimethylammonium]butyrate chloride (XTMAB)

3-Carboxypropyltrimethyl ammonium chloride (3.44 g, 18.9 mmol) and CDI (3.06 g, 18.9 mmol) were dissolved in 105 ml DMSO under stirring at 70 °C for 1 h. This solution was added to a solution of xylan (5.00 g, 37.8 mmol) in 30 ml DMSO. The mixture was allowed to react 20 h at 70 °C. The product was precipitated in acetone, washed four times with 100 ml acetone, dissolved in water and dialyzed against water (MWCO 500–1000 D), and freeze dried. Yield: 6.23 g, light brown colour. Elemental analysis (w/w%): C: 44.30, H: 7.27, N: 2.23, Cl: 4.63. DS 0.32 (DS_{Ac} 0.39), M_w 55,200 g/mol (0.1% trifluoracetic acid/0.05 M NaCl, pullulan as standard). ^{13}C NMR spectroscopy (D_2O) δ(ppm) = 173.8 and 173.3 (C=O), 102.4 (C1), 99.9 (C1′), 77.0–70.9 (C4, C3, C2), 65.4 (C8), 63.0 (C5), 53.1 (C9), 30.3 (C6) 20.4 (C10), 17.9 (C7). Numbering of the atoms according structure in Fig. 1.

2.4. Characterization of PHWE xylan and its derivatives

The sugar composition of the xylan was determined by HPLC after complete chain degradation according to Heinze, Erler, Nehls, and Klemm (1994) and Heinze, Pfeiffer, Liebert, & Heinze (1999). Briefly, 100 mg polymer was hydrolyzed with 2 ml 70% (v/v) $HClO_4$ within 10 min at 25 °C, and after dilution with 18 ml water during for 16 h at 100 °C. The samples were carefully neutralized with 2 M aqueous KOH solution. To guarantee a complete precipitation of $KClO_4$, the samples were kept at 4 °C for 1 h, and subsequently the solution was concentrated to 4 ml. The samples (20 μL) were analyzed by means of HPLC (KNAUER): column 1 Phenomenex Rezex ROA, column 2 Bio-Rad Aminex HPX-87H, 0.5 ml/min, 0.05 M H_2SO_4, an intelligent pump (KNAUER HPLC pump 64), a differential refractometer (KNAUER), and HPLC software (BOR-WIN) (Heinze et al., 1994, 1999). The uronic acids were analyzed according to Willför et al. (2009), using gas chromatography after acid methanolysis followed by silylation of the extracted xylan.

The molar mass, and the molar mass distribution of the starting xylan was determined by size exclusion chromatography in DMSO/LiBr (system from Jasco with SEC-pump PU-980; RI detector (RI-930); columns: NOVEMA 3000 and NOVEMA 300; flow rate: 0.5 ml/min; temperature: 65 °C). The molar mass, and the molar mass distribution of the cationic xylan was studied in 0.1% TFA/0.05 M NaCl solution (system from Jasco with SEC-pump PU-980; RI detector (RI-930); column: PSS SUPREMA-MAX pre/300 Å; flow rate 1 ml/min; temperature: 30 °C) while the anionic XDs were investigated in 0.1 M Na_2HPO_4/NaN_3 aqueous solution (system from Jasco with SEC-pump PU-980; RI detector (RI-930); column: PSS SUPREMA 100/1000/100 Å for 0.1 M Na_2HPO_4/NaN_3: flow rate: 0.5 ml/min, temperature: 30 °C). The samples were dissolved in the eluent with a concentration of 1 g/l and 100 μL of these solutions were injected except the XTMAB solution, which was injected with 50 μL. The calculation was done with software WinGPC (Polymerstandardservice, PSS Mainz, Germany) with pullulan standard.

The degree of substitution (DS) of the carboxymethyl xylan was determined after hydrolytic chain degradation by HPLC (Petzold, Schwikal, & Heinze, 2006). The DS of the xylan sulfate and xylan 4-[*N*,*N*,*N*-trimethylammonium]butyrate chloride (XTMAB) was calculated from the elemental analysis (Vario ELIII, Elementaranalysensysteme, Hanau, Germany).

The ^1H and ^{13}C NMR spectra were measured on a 250 MHz spectrometer (AVANCE 250, Bruker) or 400 MHz spectrometer (Avance 400, Bruker) in an appropriate solvent.

2.5. Sorption experiments and fibre modification

Sorption experiments were performed using bleached pine Kraft pulp as substrate (bleaching sequence DO-EOP-D1-P; brightness of 86). A 0.8 mg/ml polymer aqueous solution (I) was prepared by dissolving the XDs in a 10^{-5} M sodium bicarbonate aqueous solution (II). Different volumes of I and II were mixed for preparing

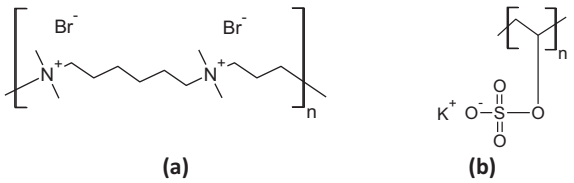


Fig. 2. Structure of polybrene (a) and structure of potassium poly(vinyl alcohol) sulphate, KPVS (b).

20 ml of XD solutions with different concentration. Then, 100 mg of bleached pine Kraft pulp (based on dry weight) was added to the prepared solutions and mixed in Schott glass bottles. Two blanks were prepared in the same way, with no addition of pulp (blank B1) and no addition of xylan polyelectrolyte (blank B2). After 16 h of vigorous stirring at 25 °C in a closed system, the samples were filtered under vacuum through glass microfiber filters (Whatman GF/A). The modified pulps were kept onto the cold room until further analysis and the filtrates were immediately titrated.

2.6. Quantification of the sorbed amount of XDs

The sorbed amount of XDs was estimated using subtractive method based on titration of the XD solutions. The sorbed amount of XD was calculated from the difference in consumed volume of titrant for the XD solution before contact with the pulp, and after filtration once the experiment ended. The titrations were performed using a particle charge detector Mütek PCD 03 (Mütek Analytic GMbH, Herrsching) with a separate automatic dispenser. As a titrant for XS and CMX, a 0.0005 N polybrene solution (see Fig. 2a) was used, meanwhile 0.001 N potassium poly(vinyl alcohol) sulfate solution (see Fig. 2b) was used as a titrant for XTMAB.

Calibration curves were prepared in order to analyze the correlation between *volume of titrant* and the concentration of *XD solution*. A typical calibration curve is presented in Fig. 3. Sorption isotherms were prepared with the collected data after sorption experiments.

2.7. Surface characterization

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) and X-ray photoelectron spectroscopy (XPS or ESCA) were used as spectroscopic techniques for characterization of the pulp treated with the positively charged polyelectrolyte, XTMAB.

Secondary ion mass spectra were obtained using a physical electronics ToF-SIMS TRIFT II spectrometer. A primary ion beam of $^{69}Ga^{+}$ liquid metal ion source (LIMS) with 15 kV applied voltage

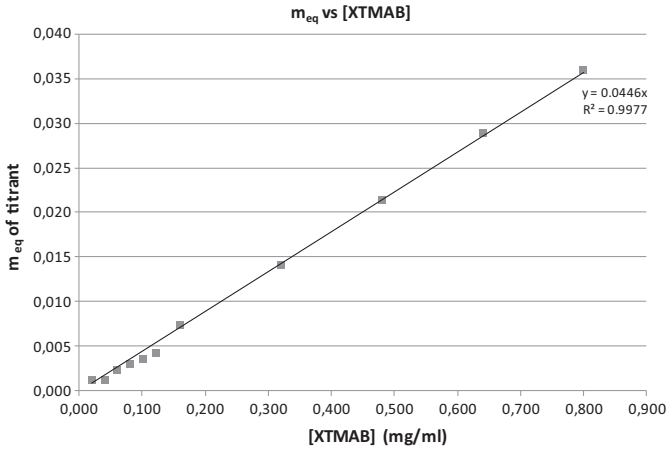


Fig. 3. Calibration curve for XTMAB. Milliequivalents of KPVS versus the concentration of XTMAB solution later used in sorption experiments.

was used in both positive and negative modes. A raster size of 200 × 200 μm was scanned and at least three different spots were analyzed. The surface distribution of XTMAB was obtained with the best spatial resolution using the ion gun operating at 25 kV. The spectra were acquired for 8 min ensuring static conditions. Charge compensation was obtained with an electron flood gun pulsed out of phase with respect to the ion gun.

The positively charged xylan derivative was characterized by using ToF-SIMS. Solutions (0.8 mg/ml) of xylan and XTMAB were prepared by dissolving the polymers in deionized water. These solutions were dropped on MN 640 w filter papers (Macherey-Nagel GmbH and Co. KG, Düren, Germany) yielding "sample 1" (xylan) and "sample 2" (XTMAB) respectively.

XPS spectra of pulp surfaces were obtained with a Physical Electronics PHI 5500 ESCA instrument equipped with a monochromatic Al K X-ray source, operated at 200 W and with an electron flood gun for charge compensation. The detector position was at an angle of 70° in relation to the sample surface. The analyzed area was 1 mm^2 and at least three different spots were measured on each sample in order to determine the analytical variations. The surface anionic groups on the fibres surfaces was estimated by labelling the pulp with methylene blue (MB) and subsequent analysis of this labelled pulp by using XPS as is described by Fardim and Holmbom (2005). The analyzed sample was chosen from a set of samples of the original pulp saturated with MB, and the study was done for only one sample and three measuring points.

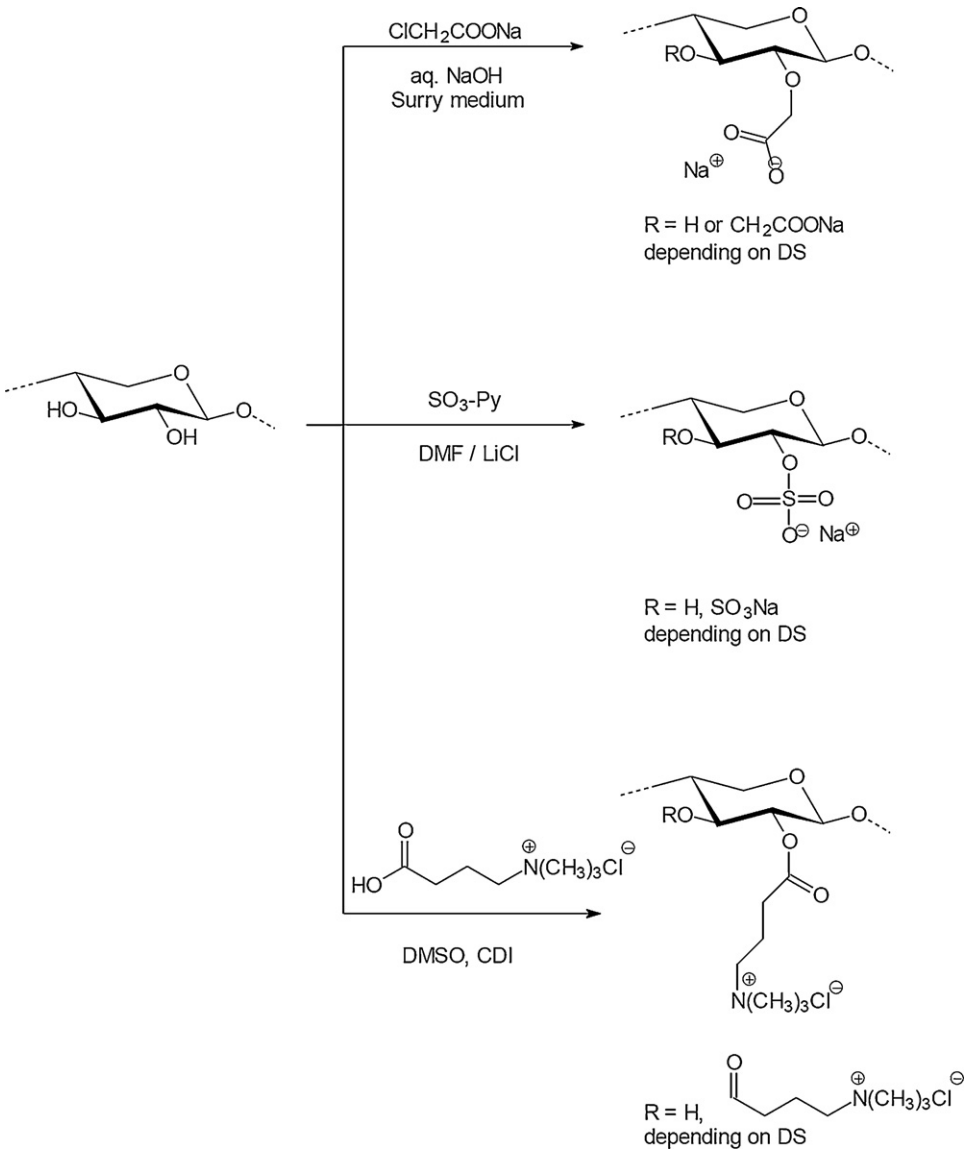
3. Results and discussion

3.1. Chemical characterization of xylan and xylan derivatives

The pressurized hot water extracted xylan has a sugar composition of 73.0% xylose, 10.1% glucose, 4.2% rhamnose and 12.6% of not identified sugars that were calculated from the HPLC chromatogram obtained after hydrolytic chain degradation. The extracted material contains 2.9% of 4-O-methylglucupyranosyluronic acid, 4.1% of galacturonic acid, and 0.7% of glucuronic acid according to the calculations from GC analysis. The isolated xylan is still acetylated with a DS_{ac} of 0.39. The NMR spectra (spectra not shown) possess the typical signals for a hardwood xylan (Petzold, Günter, Kötteritzsch, & Heinze, 2008). Thus, in the ^{13}C NMR spectrum, C1 signals were detected for internal anhydroxylose units as well as for end groups (103.8–100.0 ppm). At 97.9 ppm, the signal of the C1 of the 4-O-methylglucupyranosyluronic acid was determined. The signals of the carbons 2–4 of the anhydroxylose units were obtained in the range of 68–78 ppm. The C5 signal was found at 63.7 ppm. The signal of the carbon atom of the methyl substituent from the 4-O-methylglucupyranosyluronic acid side group was observed at 60.9 ppm. The signals of the acetyl substituent were detected at 21.4 ppm (methyl) and at 169.9 ppm (C=O).

The synthesis of the xylan derivatives was carried out by the procedures shown in Scheme 1 without a deacetylation prior to the reaction. The XS with a DS of 0.16 was synthesized by conversion of the xylan with sulfur trioxide pyridine complex (0.5 mol per mol of anhydroxylose unit, AXU) in DMF/LiCl. For synthesis of CMX, xylan was slurried in a 2-propanol followed by the addition of aqueous NaOH (15%, w/v) and sodium monochloroacetate (0.5 mol/mol AXU). The reaction was carried out for 5 h at 55 °C. The obtained CMX with a DS of 0.50 is deacetylated by the reaction under the alkaline conditions.

By the conversion of xylan with 3-carboxypropyltrimethyl ammonium chloride (0.5 mol/mol AXU), the novel cationic xylan ester XTMAB was obtained. The 3-carboxypropyltrimethyl ammonium chloride was allowed to react with CDI for activation, forming



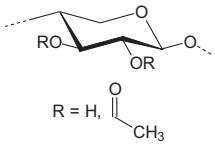
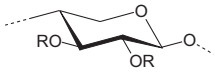
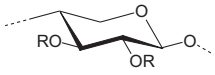
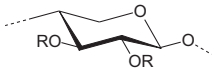
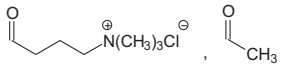
Scheme 1. Paths for the synthesis of ionic xylan derivatives illustrated using an idealized xylan.

the imidazolide of the acid (Heinze et al., 2006). The imidazolide was allowed to react with the xylan to form XTMAB with a DS of 0.32. Under the used condition, the acetyl content of the starting xylan was sustained.

As expected, the xylan derivatives were soluble in water and insoluble in the aprotic solvents tested like DMSO or DMF.

Table 1 summarizes the average molar mass of compounds measured by size exclusion chromatography (SEC), and their estimated degree of polymerization (DP). The samples were measured in different eluents regarding their solubility. Thus, the xylan was analyzed in DMSO/LiBr. The anionic samples XS and CMX were investigated in aqueous solution containing 0.1 M Na_2HPO_4/NaN_3. The cationic XTMAB were studied in 0.1% trifluoroacetic acid/0.05 M NaCl solution. So, a comparison is difficult but a tendency could be reasoned. The xylan has an M_w of 10,700 g/mol resulting in a DP of 72. The higher M_w value of the xylan than reported in the literature (Borrega et al., 2011) is mainly a result of the short extraction time (10 min) in combination with a lower temperature (160 °C). Furthermore, using the described PHWE procedure a very low yield was obtained, which could be a result of a washing out effect of the low-molar mass xylans. The XS and the CMX have M_w values in the same range (16,300 g/mol and 16,200 g/mol, respectively), which results in DP values of 110 for XS and 94 for CMX. It seems that no chain degradation occurs under the reaction conditions used because the theoretical M_w of XS should be 10,626 g/mol, and for CMX 12,384 g/mol. The XTMAB possesses a M_w of 55,200 g/mol and a DP of 276 under the used analysis conditions. It seems that aggregates of 2–4 molecules occur in the solution used for SEC, because the theoretical calculated M_w should be 14,400 g/mol. Further investigations on molar mass determination of XTMAB with SEC with 0.1% trifluoroacetic acid and higher concentration of the salt (0.3 M NaCl) have shown that a lower value of M_w of 33,700 g/mol (DPw 168) can be observed. This may be caused by a higher shielding of the ionic groups from the cationic polyelectrolyte, which also effects an improved formation of a random coil conformation. Chain degradation under the esterification conditions used for synthesis of XTMAB could not be detected. Since the calibration of the SEC measurement was carried out with the uncharged pullulan as standard, the results of the molar mass determination have to be handled with care. To suppress the influence of the polymer conformation, the polyelectrolytes were measured in a salt solution to get a random coil.

Table 1
Weight average molar mass (M_w), degree of polymerization (DP) and polydispersity (PDI) of pressurized hot water extracted xylan and xylan derivatives determined by size exclusion chromatography.

Sample	Structure	DS	M_{RU}[a] [g/mol]	M_w [g/mol]	DPw[b]	DPI
Xylan[c]		0.39 (acetate)	148	10,728	72	2.1
XS[d]	 R = H, SO_3Na	0.16	148	16,314	110	1.5
CMX[e]	 R = H, CH_2COONa	0.50	172	16,153	94	2.0
XTMAB[f]	 R = H, 	0.32 (0.39 acetate)	200	55,236[g]	276[g]	1.7

[a] Molar mass of repeating unit, $M_{Ru} = 132\,g/mol - DS \cdot M_H + DS \cdot M_{Sub}$.
[b] $DP_w = \frac{M_w}{M_{Ru}}$
[c] Xylan was measured in DMSO/LiBr
[d] Xylan sulfate, measured in 0.1 M Na_2HPO_4/NaN_3
[e] Carboxymethyl xylan, measured in 0.1 M Na_2HPO_4/NaN_3
[f] Xylan-4-[*N*,*N*,*N*-trimethylammonium]butyrate chloride, measured in 0.1% trifluoroacetic acid/0.05 M NaCl.
[g] Probably aggregates affect SEC results.

The structure of the xylan derivatives was characterized by means of NMR spectroscopy. XS ^{13}C NMR spectrum showed the typical peaks of xylan sulfate (spectrum not shown). In the ^{13}C NMR spectrum of the CMX in D_2O, the signal of the carboxyl carbon of the carboxymethyl substituent was detected at 178.5 ppm. For C1, a strong signal was determined at 101.3 ppm that corresponds to the signal of C1 neighboured to unsubstituted position 2. Additionally, a weak signal at 99.7 ppm appeared corresponding to the C1′ atom neighboured to a carboxymethylated position 2. The peaks for the C2 and C3 atoms of the carboxymethylated positions 2 and 3 occurred in the region 83.4–80.0 ppm. The signal of C2 and C3 of unsubstituted positions 2 and 3 as well as C4 appear in the region from 76.5 to 71.7 ppm. The signal of the carbon of the methylene group of the carboxymethyl moiety was detected at 70.9 ppm as proved by DEPT 135 NMR spectroscopy. The C5 signal was identified at 63.1 ppm.

Fig. 1 shows the ^{13}C NMR spectrum of the novel xylan derivative XTMAB, which proves the structure of the cationic ester as well as the preservation of the original acetate moieties of the starting xylan. All signals of the substituents were identified. The signals of the carbonyl carbons of the TMAB and the acetate substituents were detected at 173.8 and 173.3 ppm. The signal of C1 is split off depending on the neighboured position 2. If the position 2 is unsubstituted, the C1 signal appears at 102.4 ppm, on one hand. On the other, in case of substituted position 2, the C1′ signal occurs at 99.9 ppm. Additional splitting of the C1 signal seems to be reasoned in the manifold of the possible repeating units, e.g. internal, reducing end, non-reducing end (Daus et al., 2011; Petzold et al., 2008). The signals of the atoms of C2 to C4 were determined in the region from 77.0 to 70.9 ppm. The C5-signal was detected at 63.0 ppm. The signal of C8 atom of the methylene group neighboured to the ammonium group of the TMAB moiety was identified at 65.4 ppm. The methylene carbon C6 neighboured to the carbonyl group was found at 30.3 ppm. The peak of the carbon C7 of the "middle" methylene group appeared at 17.9 ppm. The signal of the carbons C9 of the methyl groups of the ammonium moiety was determined at 53.1 ppm. The methyl carbon of the acetyl moiety occurred at 20.7 ppm (C10). The signal of the carbon atom of the methyl substituent of the 4-O-methylglucupyranosyluronic acid side group was found at 60.1 ppm.

3.2. Sorption experiments

Sorption experiments for XS, CMX and XTMAB were performed using bleached pine Kraft pulp as substrate. Sorption isotherms show the amount of sorbed XD per 100 mg of pulp (based on dry weight) versus the amount of XD still in solution after adsorption (expressed in milli-equivalents), which is named "m_{eq} free". The saturation level on the sorption isotherms represents the maximum amount of XD that can be adsorbed on the fibres or equivalently, the minimum amount of XD which is needed for saturating the fibres surface. For the present work, the saturation level represents a measure of the total charge that can be adsorbed onto the fibres.

As shown in Fig. 4, XTMAB stays attached to the fibres and a saturation level is reached when 70 μeq of XD per gram of pulp or more is used. The value can also be expressed as 70 μmol/g, since the cationic functional group is monovalent.

Regarding to the DS of 0.32 for the cationic xylan derivative, is possible to estimate that 70 μmol corresponds to 0.044 g of compound. Thus, this should be the minimum amount of XTMAB that is needed to saturate one gram of pulp (based on dry weight). The estimated value is very close to the minimum amount of XTMAB that was used at the sorption experiments in order reach the saturation level.

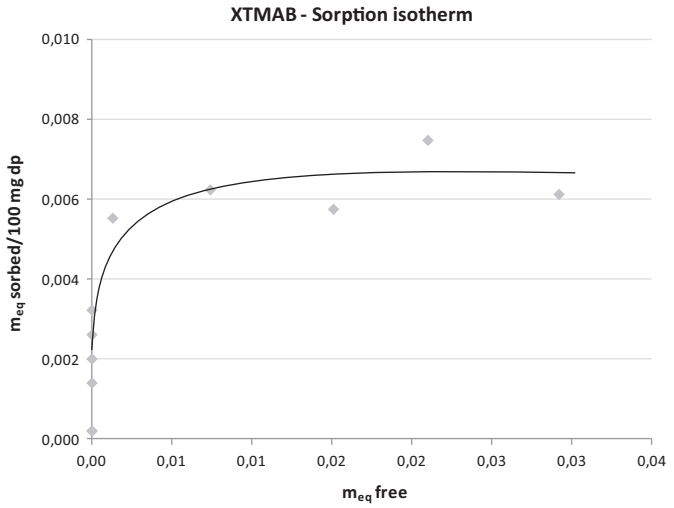


Fig. 4. Sorption isotherm showing the amount of xylan-4-[*N*,*N*,*N*-trimethylammonium]butyrate chloride (XTMAB) per 100 mg of bleached pine Kraft pulp versus "m_{eq} free" representing the amount of XTMAB still in solution after sorption.

Since the bleached pine Kraft pulp had XTMAB sorption of the Langmuir type, the assumptions sustained by a Langmuir interaction may be considered. Langmuir model assumes uniformity for adsorbent surface, no interaction between adsorbed molecules, the same mechanism of the all adsorptions, and only a monolayer formed at the maximum adsorption level. In other words, it seems that a specific adsorption of XTMAB on the charged sites in fibres occurred, despite the heterogeneity in chemistry, character of AGs and surface roughness that is present in the used pulp.

On the other hand, no sorption of XS and CMX onto the pulp takes place (data not shown). These results are consistent with our expectations, since negatively charged polymers might not significantly be adsorbed onto a negatively charged surface due to electrostatic repulsions.

3.3. Surface characterization

3.3.1. Surface characterization by XPS

The surface anionic groups (SAG) value – on the fibre surface – was estimated by labelling the fibres with MB and subsequent analysis by using XPS. The value was calculated according to Eq. (1):

$$\mathrm{SAG} = \frac{\mathrm{S}(32.06)}{[\mathrm{C}(12.00) + \mathrm{O}(15.99) + \mathrm{N}(14.00) + \mathrm{S}(32.06)]} \times \left[\frac{1}{32.06} \times 10^6\right] \quad (1)$$

where S, C, N, and O, are the amounts (measured by ToF-SIMS and expressed in atomic percentage) of sulphur, carbon, nitrogen, and oxygen respectively. SAG value, represents the amount of anionic groups at the pulp surface (3–10 nm depth). The resulting SAG value for the untreated pulp used in the sorption experiments was 73 μmol/g. The standard deviation of three measured points was 0.2.

The SAG value calculated by XPS is very close to the saturation level from the sorption isotherm showed on Fig. 4. Therefore, the amount of anionic groups at the pulp surface is very similar to the maximum amount of cationic groups that can be adsorbed onto the fibres surface. This similarity strongly suggests that the sorption of XTMAB is done onto the fibre surfaces mainly driven by electrostatic forces.

3.3.2. Surface characterization by ToF-SIMS

ToF-SIMS spectrum for the "sample 1" (spectrum not shown) possesses the characteristic peaks for xylan and cellulose. A peak with $m/z = 115$ corresponding to $[C_5H_7O_3]^+$ ion is observed showing a high intensive signal. On the other hand, the fragmentation pattern obtained from the "sample 2" (spectrum not shown) possesses two peaks with high intense signal at $m/z = 58$ and $m/z = 146$. These peaks were assigned to $[H_2C{=}N^+(CH_3)_2]$ and $[HOOC(CH_2)_3N^+(CH_3)_3]$ ions and were selected for subsequent analysis of the modified pulp with XTMAB.

The pulp from "blank B2" was also analyzed by ToF-SIMS. Typical fragmentation pattern was shown on the spectrum for the unmodified pulp. Again, a characteristic signal was detected at $m/z = 115$ while neither significant signals at $m/z = 58$ nor $m/z = 146$ were registered (Fig. 5).

Finally, the spectrum for the modified fibres surface (after treatment with XTMAB) showed very intense signals at $m/z = 58$ and $m/z = 146$ confirming the presence of XTMAB onto the fibres surface (Fig. 6).

In addition, ToF-SIMS imaging was used to study the distribution of the XTMAB onto the fibre surfaces (Fig. 7) by monitoring

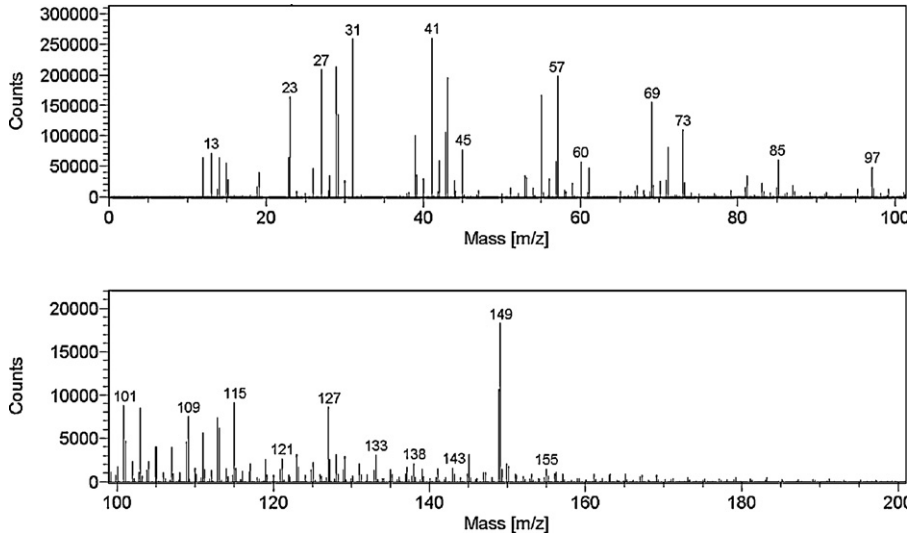


Fig. 5. ToF-SIMS spectrum of the non-modified bleached pine Kraft pulp.

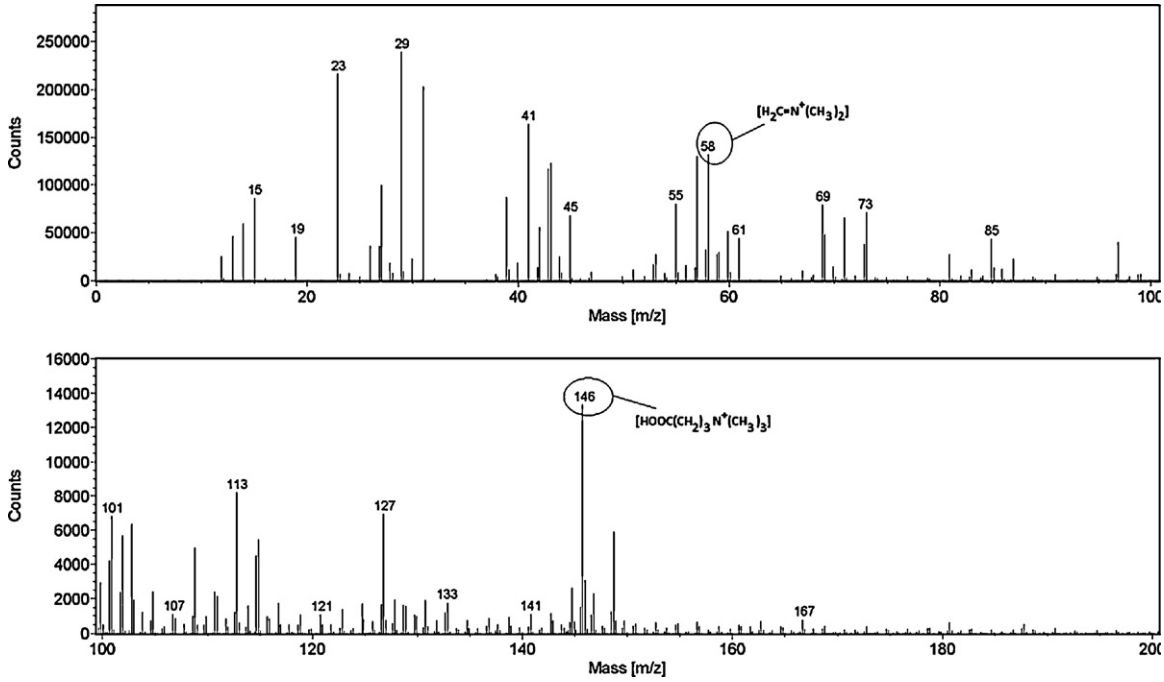


Fig. 6. ToF-SIMS spectra of the pulp modified with xylan-4-[*N*,*N*,*N*-trimethylammonium]butyrate chloride (XTMAB).

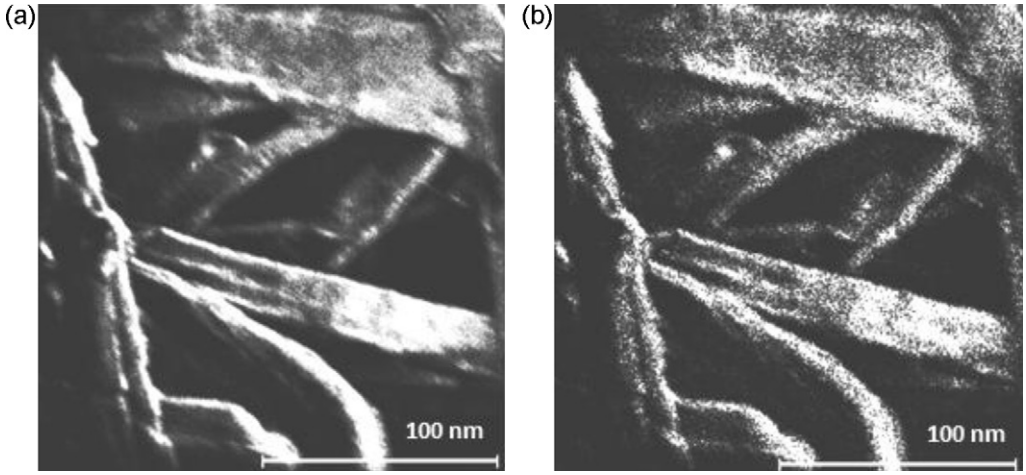


Fig. 7. ToF-SIMS images in positive mode of total secondary ions for a transverse section of bleached Kraft pulp treated with xylan-4-[*N*,*N*,*N*-trimethylammonium]butyrate chloride (XTMAB) (a) and XTMAB characteristic ions with signal at $m/z = 58$ and $m/z = 146$ for the same sample (b).

$[H_2C{=}N^+(CH_3)_2]$ and $[HOOC(CH_2)_3N^+(CH_3)_3]$ ions. As shown in Fig. 7b, the surface distribution of the XTMAB polymers on the fibres was quite homogeneous and the polymer is covering evenly the surface.

4. Conclusions

Xylan was isolated from birch chips by using pressurized hot water extraction at 160 °C. According to SEC results, a DP close to 70 repeating units showed that molecular structure of the extracted xylan is fairly well preserved in comparison with the native xylan that constitutes the birch wood, which DP is assumed to be close to 100. Three derivatives were prepared using the extracted xylan as starting material and further characterized regarding structure and solubility. The DSs of the prepared derivatives were: 0.16, 0.32 and 0.52 for XS, XTMAB, and CMX, respectively. The prepared xylan derivatives were used as fibre modifying agents in sorption experiments. Sorption isotherms showed that the novel cationic xylan ester XTMAB was adsorbed onto the pulp fibres following Langmuir model, while no significant sorption was observed when CMX or XS were used. The SAGs on the fibres of the untreated bleached pine Kraft pulp were determined by labelling the fibres with MB and subsequent analysis by XPS. The calculated SAGs value calculated by XPS was similar with the amount of sorbed XTMAB estimated by polyelectrolyte titration, which strongly suggest that the sorption occurred at the surface of the fibres.

XTMAB, untreated bleached pine Kraft pulp and treated pulp with XTMAB as well as a blank B2 were analyzed for the first time by ToF-SIMS. The spectrum from XTMAB showed two intense signals from ion fragments that were associated with $[H_2C{=}N^+(CH_3)_2]$ and $[HOOC(CH_2)_3N^+(CH_3)_3]$ ions. The comparison of the fragmentation patterns observed on ToF-SIMS spectra for the blank B2 and the pulp modified with XTMAB confirms that the positively charged polyelectrolyte was sorbed onto the fibres surface. According to

ToF-SIMS imaging, the sorbed XTMAB was evenly distributed onto the fibres surface.

Our experiments confirmed that a positive polyelectrolyte prepared from extracted xylan, could be used as a modifying fibre surface agent. The modification of fibre surfaces by using xylan derivatives represents the "starting point" for our studies in searching a better use of the natural polymers and contributes to a better understanding of the interaction between pulp fibres and charged polymers.

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