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Effects of cationic xylan from annual plants on the mechanical properties of paper

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ABSTRACT

Xylan from oat spelt and wheat was used as an additive to enhance the dry strength of paper. The absorption of xylan by the cellulose fibers was increased by cationization to different degrees of substitution. Paper hand sheets with different doses of xylan and industrial cationic starch were produced, and the mechanical properties were determined. Absorption measurements of cationic oat spelt xylan on pulp fibers explained the differing influences of low and high cationized xylan addition on paper strength. The addition of cationic oat spelt xylan with a degree of substitution of 0.1 at a 4% dose provided the largest improvement in the tensile-index (67%), burst-index (105%) and tear-index (77%). Compared to cationic starch, cationic oat spelt xylan additives led to similar paper strength values, excepting the tear strength. The structural differences and protein impurities made the wheat xylan unsuitable as a strength additive for paper pulp.

1. Introduction

Due to the increasing shortage of fossil resources and increased environmental awareness, sustainable bio-based materials have gained increased attention in research and product development. Hemicelluloses, particularly xylans, appear in concentrations above 30% in agricultural by-products such as husks and straw (Ebringerova, Hromadkova, & Heinze, 2005; Puls, Schroder, Stein, Janzon, & Saake, 2006). Currently, these raw materials are used predominantly as low-value additives for animal feed; however, numerous high-value applications for polymeric xylans have been developed on the laboratory-scale. Various authors report that xylans may be used as a strength-increasing paper additive (Han et al., 2012; Ramirez, Puls, Zuniga, & Saake, 2008; Saake, Busse, & Puls, 2005; Westbye, Kohnke, Esker, Glasser, & Gatenholm, 2006). Xylan films are a good oxygen barrier, suggesting possible applications in food packaging (Grondahl, Eriksson, & Gatenholm, 2004; Hansen & Plackett, 2008). Furthermore, xylans and their derivatives have been successfully tested as thermoplastic materials (Fang, Sun, Fowler, Tomkinson, & Hill, 1999; Glasser, Jain, & Sjostedt, 1995). However, none of these new polymeric applications have been exploited on the industrial scale because no reliable technical xylan sources have managed to provide consistent quality and sufficient quantities. Currently, the only industrial-scale xylan source is the steeping-lye from the viscose process that produces dissolving pulp from hardwoods (Griebl, Lange, Weber, Milacher, & Sixta, 2006). Polymeric xylan may be more easily extracted from agricultural residues than wood because wood contains more lignin and the xylan is integrated strongly into the lignified tissue (Ebringerova et al., 2005; Fengel & Wegener, 1984). Therefore, delignification is necessary to obtain xylan via extraction from wood when high yields are required. Many alkaline extraction processes for raw materials derived from annual plants have been patented in recent years. For oat spelt, a roller mill treatment was developed to increase the efficiency of alkaline extraction with NaOH (Kahlke, 2006). In this process, an arabinoxylan with a DP (degree of polymerization) between 200 and 220 could be isolated (Saake, Erasmy, Kruse, Schmekal, & Puls, 2004). The *Eastman Chemical Company* patented an alkali xylan extraction for corn fibers utilizing proteases for purification (Buchanan, Debenham, Shelton, & Wood, 2002). After the NaOH extraction, a high molecular weight fraction (>50,000 g/mol) and a low molecular weight fraction (<25,000 g/mol) composed of arabinoxylans was obtained (Buchanan et al., 2002). Water-based methods for arabinoxylan extraction from annual plants have also been investigated (Hollmann & Lindhauer, 2005; Maes & Delcour, 2002). Jäckering patented a process to extract arabinoxylan from an aqueous flour suspension using centrifugation and enzymatic treatment. This

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process enables industrial-scale xylan extraction without alkali (Roick, 2011).

Xylans contribute to the properties of paper-grade pulp and paper. In contrast to dissolving pulp production, a high xylan concentration is desirable for paper grade pulp to increase the pulp yield and strength properties. The subsequent addition of isolated xylan during the paper making process may improve mechanical properties (Bai, Hu, & Xu, 2012; Ramirez et al., 2008). Because carboxylate groups are introduced by the pulping and bleaching processes, the cellulosic fibers carry a slightly negative charge (Potthast et al., 2003; Schleicher & Lang, 1994). These negative charges cause electrostatic repulsion between the single "anionic" fibers and decrease the possible inter-fiber linkages (Bos, 1999; Schwikal et al., 2011). The absorption of cationic additives, such as starch or xylans, onto the anionic pulp surface decreases the electrostatic repulsion effect and therefore enhances the inter-fiber linkages and mechanical properties (Fatehi, 2011; Ghasemian, Ghaffari, & Ashori, 2012; Silva et al., 2011). A common derivatization agent used to add cationic groups to paper additives is 2,3-epoxyproplytrimethylammonium chloride. Cationic side groups lead to higher additive retention; however the number of cationic groups is not directly proportional to the mechanical properties of the paper (Pelton, 2004; Zhang, Pelton, Wagberg, & Rundlof, 2001). A slight cationization of birch xylan to a degree of substitution of 0.1 causes an increase in tensile and tear strength of up to 60%. Lower or higher cationization of the birch xylan causes inferior performance (Schwikal et al., 2011).

Former studies on cationic xylans used as a strength additive for paper focused on xylans from wood (Schwikal et al., 2011). In this study cationic xylans extracted from wheat flour and oat spelt were used. The isolation of xylan from wood in high yields requires a delignification while for agricultural residues a direct extraction can be realized. Therefore, these xylans have higher chances for industrial implementation. Further on, the raw materials are wastes or by-products, which are not in competition with material, energy or food use of the biomass. In addition, xylans from annual plant sources consist of a different molecular structure than wood xylan and may have therefore a different effect on the paper strength. The aim of this study was to elucidate the correlations between the cationic charge of the xylans, their absorption behavior and the resulting mechanical properties of paper. Therefore, various cationized oat and wheat xylans (DS 0.012–0.325; degree of substitution) were produced and combined in the range of 0.25–6% with eucalyptus pulp to produce hand sheets. Subsequently the mechanical properties of various test sheets were determined by measuring tensile-, tear- and burst- index. The absorption of the three cationic xylans on the pulp was measured by polyelectrolyte titration after the retention experiments for doses of 1–6% xylan relative to the eucalyptus pulp.

2. Materials and methods

2.1. Materials

The oat spelts were provided by the company Peter Kölln KGaA (Elmshorn/Germany). The OSX (oat spelt xylan) was extracted with 5% NaOH at 90 °C for 2 h. The precipitation and washing of the OSX was performed in methanol. The wheat xylan (WX) was provided by a cereal company: Jäckering (Hamm/Germany), where the WX was directly extracted from flour suspension during starch production (Roick, 2011).

Three cationic starches were supplied by Cargill (Krefeld/Germany): C*Bond HR 05946 (corn starch, DS 0.05), C*iBond 25955 (wheat starch, DS 0.04) and C*Bond HR 35845 (potato starch, DS 0.05).

A bleached eucalyptus kraft pulp from Aracruz (São Paulo/Brazil) was chosen for the paper making process. The pulp was beaten with a laboratory refiner to SR 25 and had a brightness of 88% ISO. The carbohydrate composition consisted of 85% glucose and 15% xylose.

2.2. Synthesis of cationic xylan

The synthesis of the cationic xylans was performed with 2,3-epoxyproplytrimethylammonium chloride (EPTA) from the TITK (Rudolstadt/Germany). The chosen ratios of EPTA to anhydroxylose unit (AXU) were from 0.075:1 to 0.5:1. The detailed derivatization procedure was published previously (Schwikal et al., 2011).

2.3. Analysis of additives

The carbohydrate compositions of unmodified xylans were determined after a mild 1-step hydrolysis using 0.5 M H_2SO_4 at 120 °C and 1.2 bar for 40 min. Subsequently the monosaccharide contents were determined using borate complex anion exchange chromatography as described previously (Sinner & Puls, 1978; Sinner, Simatupang, & Dietrichs, 1975). The determination of the uronic acid content was performed at 80 °C in NaOD (1%, w/v) using ^{1}H NMR with a pulse angle of 45° and a relaxation delay of 12 s; the signals were evaluated according to Teleman et al. (1995). The molar mass data of the xylans were determined using size exclusion chromatography with DMSO:water (9:1) and a 0.05 M LiBr additive, as published previously (Saake, Kruse, & Puls, 2001). The enzymatic degradations were performed with 10 mg of unmodified xylan in 0.975 ml ammonium acetate/acetic acid buffer at pH 4.9 with a addition of 25 μl xylanase (NS22036, Novozymes, Bagsvaerd/Denmark) at 60 °C for 24 h in a Thermomixer comfort (Eppendorf AG, Hamburg/Germany). The xylanase activity of 42,040 nkat/ml was determined by the company ASA special enzymes GmbH (Wolfenbüttel/Germany). The ash content of each additive was determined according to TAPPI T 211 om-02 at 525 °C. The molar degree of substitution for the cationic starches was reported by the manufacturer. For the cationic xylans, the DS was calculated using the nitrogen and carbon content measured by elemental analysis (vario EL cube, Elementar Hanau/Germany). The samples will be named in the following with the DS value (OSX with a DS of 0.07 will be named OSX 0.07). According to Schwikal et al. (2011), the DS calculation for xylans requires the following equation:

$$\mathrm{DS} = \frac{60 \times w(N)}{14 \times w(C) - 72 \times w(N)}$$

The charge density of the cationic xylans was measured with an automatic titration unit (Titrino basic, model 794, Metrohm, Filderstadt/Germany) at pH 7. Before titration, 100 mg_{atro} cationic xylan was homogenized in 100 ml hot (99 °C) distilled water with an Ultra Turrax. Depending on the surface charge of the sample, the titrant was 0.001 M sodium polystyrenesulfonate for a cationic samples or 0.001 M diallyldimethylammonium chloride for anionic samples (Titrants: PES-Na and Poly Dadmac from Mütek BTG, Herrsching/Germany). The charge density was determined with a particle charge detector (PCD) and calculated using the following equation (Schwikal et al., 2011):

$$q[\mu \frac{eq}{g}] = \frac{V(Titrant) \times c(Titrant) \times 10^6}{V(Sample) \times w(Sample)}$$

2.4. Production of handsheets

A 4% (w/w) pulp solution was swollen overnight in distilled water and beaten with a disk refiner (Sprout-Bauer type, 12 in. disk,

Table 1
Characterization of OSX and WX.

Sample	Carbohydrate composition (%)[a]				Hydrolosis residue[b] (%)	Ash (%)	Protein[c] (%)	M_w (g/mol)	Polydispersity M_w/M_n
	Xylose	Arabinose	Galactose	Glucose					
OSX	65.8	9.1	2	3.4	3.4	17.7	0.8	24,500	1.6
WX	36.8	34.4	12.2	5.2	0.5	3.4	7.4	43,900	6.8

[a] Absolute percent based on the sample weight.
[b] Residue after 1-step acid hydrolysis.
[c] Nitrogen content was measured using elemental analysis and multiplied by 5.36 for oat and 5.33 for wheat (Mosse, 1990).

model 7208-110, 30 kW, 1500 rpm, 0.1 mm disk distance, 5 beating cycles). After beating, the pulp was dewatered to attain a 34.6% dry content by centrifugation.

Handsheets were produced with a 160 mesh screen on a Rapid-Köthen (Model type 95854, FRANK, Birkenau/Germany) according to the German Zellcheming method V/7/61. For paper-making, common tap water with a middle hardness (9.2 dh) (535 μS/cm, Ca 55 mg/l, Mg 6 mg/l) was used.

The influence of the cationic xylan additives on paper-making were measured at xylan concentrations of 0.25%, 0.5%, 1%, 2%, 4% and 6% (based on the dry weight of pulp). Five paper sheets were produced for every concentration step. Therefore, 16 g_{atro} pulp was disintegrated in 6.67 l water. According to the desired concentration levels, the appropriate amount of xylan was homogenized at 100 °C for 5 min in 150 ml distilled water and added to the pulp solution to react for 15 min before handsheet formation. One liter of this mixture (containing 2.34 g_{atro} pulp + desired xylan concentration) was used to produce one paper sheet. The amount of cationic starch added to the paper sheets was 0.25%, 1% and 2%.

2.5. Absorption of cationic xylan on the pulp fibers

The absorption of cationic xylan was measured with a particle charge detector (PCD). The amount of absorbed xylan was determined indirectly using the chemical charge of the filtrate from the paper forming process. Two other methods were also tested to measure the xylan content directly using the paper sheets. One method measured the nitrogen content of the paper sheets using elemental analysis. The other method involved a two-step sulfuric acid hydrolysis of the paper sheets and measured the sugar content by HPLC. However, with both methods it was not possible to exactly determine the amount of absorbed cationic xylan. Therefore, the subtractive PCD method was used to determine the xylan absorption on the eucalyptus pulp. For these absorption measurements, three cationic xylans with different charge densities (OSX 0.07 (219 μequiv./g), OSX 0.09 (391 μequiv./g), OSX 0.19 (729 μequiv./g)) were chosen. Because the PCD titration of the filtrates from the paper forming process generated inaccurate xylan calculations, calibration curves for each cationic xylan were prepared as follows: 5 g pulp (dry weight) were disintegrated in 1 l water with a Ultra-Turrax (Model T50, dispersion tool S 50 N – G 45 G, 5 min, 6000 rpm, company IKA, Staufen/Germany). Afterwards, the pulp was dewatered with a dynamic drainage jar (DFR-05, Mütek BTG, Herrsching/Germany, screen mesh 150). Subsequently, 1–6% xylan was added to the resulting filtrate and allowed to react with stirring for 15 min. Subsequently, the charges of the different filtrates were measured using the PCD and calibration curves were created for xylan concentrations between 1% and 6% in the filtrate.

For the actual absorption measurements, 5 g pulp were disintegrated and 1–6% of xylan was added to the production of handsheets. The pulp and xylan (total volume 1 l) were added to the drainage jar and allowed to interact with stirring for 15 min. After dewatering, the filtrate was titrated with the PCD. The amount of cationic xylan in the filtrate was calculated by using the appropriate calibration equations. To calculate the xylan absorbed on the pulp, the xylan content of the filtrate was subtracted from the initial xylan dose.

2.6. Surface charge of the xylan pulp mixture

Furthermore, the surface charge of the xylan pulp mixture was detected with a zeta-potential measuring system (SZP-06, Mütek BTG, Herrsching/Germany).

3. Results and discussion

3.1. Raw material characterization

The raw OSX and WX samples were characterized regarding their carbohydrate compositions and molecular weight data, as well as lignin, ash and protein contents (Table 1). The sugar analysis revealed that the OSX sample contained 66% xylose and 9% arabinose. Therefore, the arabinose to xylose ratio for the arabinoxylans in the OSX sample was approximately 0.1, meaning that about every tenth xylose unit in the main chain contains an arabinose group. The galactose content was 2% and most likely due to small amounts of arabinogalactan. Arabinogalactan consists of a galactose backbone attached to several arabinose and galactose side groups (Fincher & Stone, 1974; Tryfona et al., 2010). This additional hemicellulose may be covalently bonded to proteins, forming globular arabinogalactan-protein structures in the OSX and WX samples (Clarke, Anderson, & Stone, 1979; Gollner, Blaschek, & Classen, 2010). Furthermore, the OSX sample contained approximately 3% glucose because some cellulose or starch impurities were present. The hydrolysis residue of the OSX sample was 3% and can be attributed mainly to lignin, but might be partly affected by protein derived impurities. The 18% ash content was relatively high. The high ash content may be attributed to sodium residues from the extraction process caused by a precipitation event that occurs without neutralization or desalting. The WX sample had similar proportions of xylose (36.8%) and arabinose (34.5%). The high arabinose content occurs because the arabinoxylans incorporate a larger amount of arabinose side groups and numerous arabinogalactan-protein impurities (Fincher & Stone, 1974; Saulnier, Guillon, & Chateigner-Boutin, 2012). In addition to the high arabinose content, the high protein (7.4%) and galactose contents (12%) validate the presence of high arabinogalactan-protein amounts up to approximately 29% (calculated with an arabinose-to-galactose ratio of 0.8 from literature; plus the protein content) in the WX sample (Gollner et al., 2010; Loosveld, Grobet, & Delcour, 1997). Compared to OSX, the hydrolysis residue (0.5%) and ash residues (3.4%) of WX were much lower, but glucoses residues of 5% were slightly higher. The weight average molar mass (M_w) measured by SEC is 24,500 g/mol for OSX with a polydispersity of 1.6 M_w/M_n. WX had a much higher M_w (43,900 g/mol) and polydispersity (6.8).

The WX sample was extracted from the endosperm part of the wheat grain. M_w values from literature for wheat flour arabinoxylan vary between 48,700 g/mol and 319,200 g/mol (Pitkänen, Virkki, Tenkanen, & Tuomainen, 2009; Saeed, Pasha, Anjum, & Sultan, 2011). The determined M_w of the WX sample was comparable to literature M_w of low-viscosity wheat flour arabinoxylan with a low molar mass (Pitkänen et al., 2009). However, the M_w/M_n of 6.8 of the WX sample was much higher than the literature value of 1.6, which supports the assumption of impurities in the WX sample (Pitkänen et al., 2009). Molar masses reported for the arabinogalactan-proteins from cereals range between 22,000 g/mol and 120,000 g/mol and might cause the high polydispersity in the WX sample (Gollner et al., 2010; Saeed et al., 2011).

Arabinose side groups, uronic acids such as 4-O-methly glucuronic acid (MeGlcA) and glucuronic acid may be attached to some types of xylan (Ebringerova et al., 2005). Birch xylan in particular contains between 8% and 12% MeGlcA (Schwikal et al., 2011; Westbye, Svanberg, & Gatenholm, 2006). Additionally, 5.7 mol% MeGlcA was measured in the OSX sample. The analysis of the ^{1}H NMR data for the WX sample was not possible because the samples' impurities overlapped with the relevant signals. However, in the literature, many different uronic acid values for wheat xylan are reported based on where in the plant the xylan originates. Xylan extracted from wheat straw or husks may be substituted with more uronic acid (between 5% and 6%) (Akpinar, Erdogan, & Bostanci, 2009; Parker, Ng, & Waldron, 2005). Xylan originating from wheat endosperm contains little to no uronic acid (Ebringerova et al., 2005; Pellny et al., 2012; Saulnier et al., 2012). The WX sample originated from wheat grain; therefore, it was assumed that the sample contained only low amounts of uronic acids. In addition to uronic acids, ferulic acids may be attached in small amounts (0.1–0.6%) on wheat-derived xylan (Ebringerova et al., 2005; Hollmann & Lindhauer, 2005; Schooneveld-Bergmans, Hopman, Beldman, & Voragen, 1998). Because of its high arabinoxylan content (approximately 75%) and the small polydispersity (1.6), OSX is relatively homogeneous. In contrast, WX is very heterogeneous, containing only approximately 60% arabinoxylans and numerous arabinogalactan-protein structures. OSX's narrow molar mass distribution is depicted in Fig. 1a, and WX's broader molar mass distribution is displayed in Fig. 1b. A xylanase treatment was performed on both samples, causing the OSX sample to degrade more dramatically. The polymeric peak for the OSX sample decreased considerably, but the polymeric WX peak only decreased slightly. The limited degradation observed in the WX sample was most likely caused by the lower xylanase accessibility and content. WX's accessibility to enzymes was most likely hindered by the steric profile of the arabinose side groups and the arabinogalactan-protein fraction.

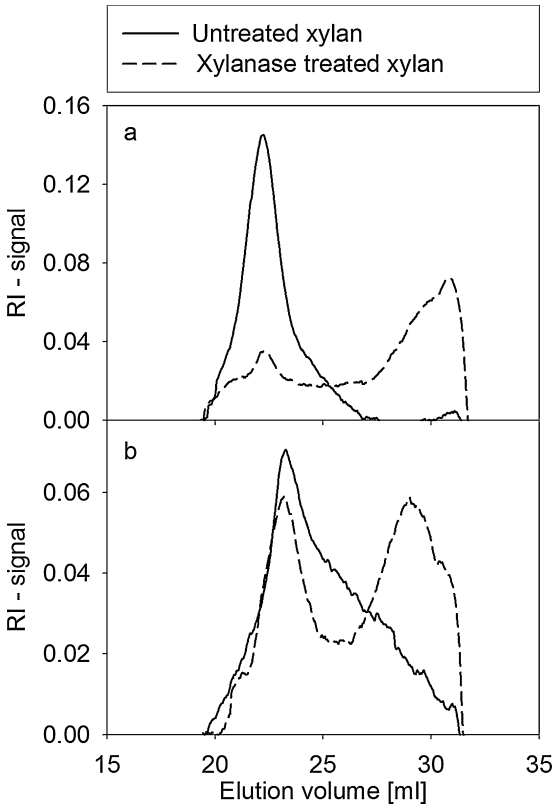

Fig. 1. SEC measurements of the molar mass distribution in OSX (a) and WX (b) before and after xylanase treatment.

3.2. Characterization of the cationic OSX and WX samples

After cationic derivatization of the OSX and WX samples, the resulting products were characterized by their charge density, DS and ash content (Table 2). Furthermore, three industrial starch products are included in Table 2 for comparison. The effectiveness of the derivatization procedure may be assessed using the charge density and the DS. The ash content provides information about the purity of cationized samples, especially regarding chlorine residues from EPTA or sodium residues from sodium hydroxide.

The OSX sample had a negative charge density (−305 μequiv./g) that may be attributed to the 5.7 mol% MeGlcA present in the sample. The WX sample only had a −88 μequiv./g anionic charge density, supporting the assumption that little uronic acid was attached to the wheat xylan. The ferulic acid content of the WX

Table 2
Characterization of the cationic samples OSX, WX and starch.

Sample name	DS	EPTA:AXU ratio	Charge density (μequiv./g)	Ash content (%)
OSX			−296.7	17.7
OSX 0.03	0.03	0.075:1	31.5	7.8
OSX 0.07	0.07	0.15:1	219.9	8.0
OSX 0.09	0.09	0.2:1	391.1	2.9
OSX 0.11	0.11	0.25:1	414.9	7.8
OSX 0.14	0.14	0.35:1	622.4	5.2
OSX 0.19	0.19	0.5:1	788.4	8.2
WX			−100.1	3.4
WX 0.01	0.01	0.075:1	33.2	14.4
WX 0.04	0.04	0.15:1	287.1	5.3
WX 0.33	0.33	0.5:1	729.4	15.2
Wheat starch 0.04	0.04[a]		129.7	2.9
Corn starch 0.05	0.05[a]		242.9	3.0
Potato stach 0.05	0.05[a]		267.2	3.2

[a] The DS of the cationic starches were given by the producing company.

sample should not influence the charge density because the acid is esterified by the xylan (Ebringerova et al., 2005; Schooneveld-Bergmans et al., 1998). The increased EPTA:AXU ratio generated during the synthesis triggered continuous increases in the charge density and DS of the OSX and WX samples. Because the lowest EPTA:AXU ratio was 0.075:1, the OSX sample had a 32 μequiv./g cationic charge density, and the WX sample had a 33 μequiv./g charge density. The highest EPTA:AXU ratio (0.5:1) generated charge densities of 788 μequiv./g for OSX and 729 μequiv./g for WX. Concurrently, the DS values increased from 0.03 to 0.19 in OSX and from 0.01 to 0.33 in WX samples. The nitrogen content attributed to the protein impurities in the xylan raw material was subtracted before the DS was calculated. However, some protein might have been removed while washing the cationized xylans. The potential extraction of proteins might influence the calculation of the DS. The ash content of the cationic OSX samples varied between 2.9% and 8%. These values are much lower than the high ash content (18%) measured for the raw OSX sample, confirming the assumption that the raw OSX's high ash content is generated by sodium residues from the NaOH extraction process (compared to raw material characterization) and might be removed during the washing step that occurs after derivatization. Ash contents between 5% and 15% were determined for the cationic WX samples. Furthermore, cationic OSX and WX samples displayed no correlation between the ETPA dose during the derivatization step and the resulting ash content. In comparison to the cationic xylan samples all three starch samples had low ash contents of approximately 3%. However, the OSX 0.09 and the WX 0.04 samples reached similar ash contents below 5%. Therefore, after a more intensive washing after derivatization, the ash content of the cationic xylans might be reduced, reaching the range found in industrial starch products.

3.3. Influence of cationic OSX and WX on mechanical paper properties

3.3.1. Comparison of cationic OSX and WX

During the initial paper testing experiments, a 4% dose xylan relative to pulp was applied to investigate the effects of oat spelt- and wheat-derived xylan on mechanical paper properties. In addition to the untreated xylans, three cationic wheat and oat spelt xylans with the EPTA:AXU ratios: 0.075:1, 0.15:1 and 0.5:1 were added respective to the pulp and the paper strength was tested. Fig. 2 depicts the results regarding the tensile-, burst- and tear-indices after the addition of cationic xylan produced with respective EPTA:AXU ratios. The reference papers had a 28 Nm/g tensile-index, a 1.5 kPa m^2/g burst-index and a 5 mN m^2/g tear-index. The addition of untreated OSX to pure eucalyptus pulp increased these mechanical properties by 22% for the tensile-index, 40% for the burst-index and 35% for the tear index. A further improvement in the tensile- and burst-index was reached by adding cationic OSX. However, no additional improvement in the tear-index was achieved by an addition of cationic OSX instead of untreated OSX. The best effect on the tensile- and burst-indices was obtained with OSX 0.07; the tensile-index increased to 38 Nm/g and the burst index increased to 2.3 kPa m^2/g. The more cationized OSX did not cause further improvement. Schwikal et al. (2011) investigated the addition of cationic birch xylan to paper. They reported that a 0.1 DS (EPTA:AXU 0.25:1) was optimal, but more functionalization caused the paper properties to decline. Compared to the pure eucalyptus pulp sheets, the hand sheets produced with WX additives displayed only slightly improved burst- and tear-indices. The best performance for WX was achieved after derivatization with EPTA:AXU 0.15:1 (DS 0,04), generating a 5.7 mN m^2/g tear-index and a 1.7 mN m^2/g burst index. For the tensile-index, adding cationic WX triggered no measurable effect. One reason for the lower performance of WX might be the arabinogalactan-protein impurities. Various authors reported that

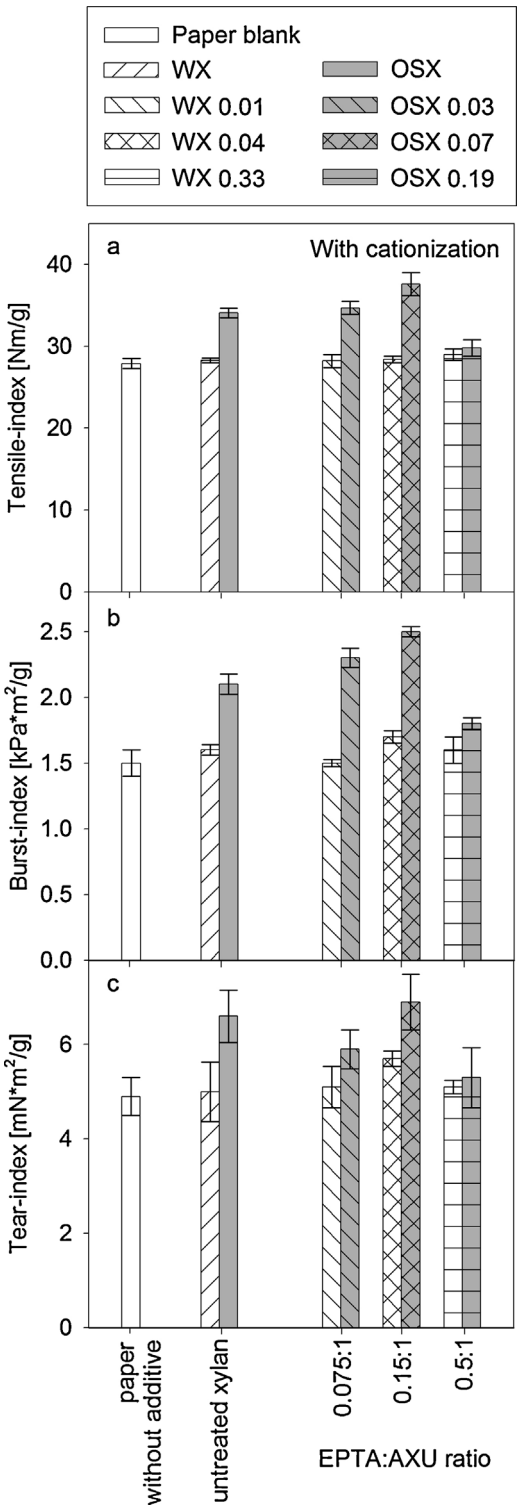

Fig. 2. Influence of oat spelt and wheat xylans with different EPTA to AXU ratios on the tensile- (a), burst- (b) and tear-index (c) of hand sheets prepared with a xylan dosage of 4%.

this structure has a globular shape according to the wattle blossom-type model (Ellis, Egelund, Schultz, & Bacic, 2010; Gollner et al., 2010). Therefore, this structure might not interact intensively with the fibers during sheet formation. The different uronic acid contents in the samples may also have influenced the paper strength. Electrostatic interactions between the cationic and carboxyl groups played a major role in improving paper strength (Schwikal et al.,

2011). In addition to the interaction between xylans cationic groups and the pulp's anionic groups, the interaction of the cationic and anionic groups within the xylans might affect the performance: the MeGlcA content in the OSX samples might cause more internal stability and better dispersion of the xylan on the fibers compared to the WX with only traces of uronic acid side groups (Ebringerova et al., 2005; Pellny et al., 2012; Saulnier et al., 2012). Therefore, an additional strength increase may be induced by OSX addition relative to the WX addition. Because only cationic OSX products furnished promising results as strength-increasing paper additives, cationic WX samples will not be considered further in this investigation.

3.3.2. Cationic OSX concentration series

During the initial tests with paper containing 4% xylan, the OSX 0.07 (0.15:1 EPTA:AXU ratio) sample exhibited the best effect on the paper's mechanical properties while inferior paper properties were observed with OSX 0.19 (0.5:1 EPTA:AXU ratio). To find the optimal cationic charge and dose for the OSX to improve the paper's mechanical properties, additional cationic OSX samples were synthesized at intermediate EPTA:AXU ratios: 0.2:1, 0.25:1, 0.35:1. These samples (OSX 0.09, OSX 0.11, OSX 0.14) were included in the concentration series. Doses above 6% are not normally used for strength enhancing additives in the paper industry. Therefore, the six cationic OSX samples were added from 0.25% to 6% to the pulp to produce the paper sheets. In Fig. 3, the percent increases in the tensile-, burst- and tear-indices of the xylan-containing papers are presented compared to paper without additives. Compared to the reference paper, adding the various cationic OSX samples increased every measured mechanical paper property. Nearly every OSX was optimally dosed at 4%, but increasing the addition to 6% decreased the mechanical properties. Only OSX 0.07 demonstrated a further increase in the mechanical paper properties at a 6% dose. The highest improvement in paper strength was reached using the OSX 0.09 sample at a 4% dose. Compared to the untreated paper, OSX 0.09 increased the tensile-index by 66%, the burst-index by 105% and the tear-index by 77%. The second best strength properties were achieved after adding cationic OSX 0.07 at a 6% dose: the tensile-, burst-, and tear-indices were increased by 56%, 101% and 88%, respectively. In conclusion, adding 4–6% cationic oat spelt xylan with a DS between 0.07 and 0.1 improved the mechanical paper properties the most.

3.3.3. Comparing cationic OSX to starch additives

Cationic starches from various materials are used in the paper industry as additives to improve dry strength. Therefore, experiments to compare cationic OSX and cationic starch as dry strength additives were conducted. For the papermaking experiments, cationic corn, wheat and potato starch were chosen; in each case, 0.25%, 1% and 2% starch were added to the pulp. The results of the addition of untreated OSX and the best performing cationic oat spelt xylan (OSX 0.09) were chosen to compare with the cationic starches. The effects of the starch and OSX addition on the relative increases in the tensile-, burst- and tear-indices of the papers were compared to the values for the untreated papers and are depicted in Fig. 4. Generally, the untreated OSX was able to increase every value, but the increase was small relative to the cationic products. At a 2% dose, adding cationic OSX 0.09 or starches caused similar enhancements in the tensile- and the burst-indices. Adding 4% OSX 0.09 to the paper sheets caused a further increase in the tensile- (up to 65%) and burst-indices (up to 100%). Only the tear-index was decreased after adding OSX 0.09 when compared to the cationic starch. The increase in the tear-index after adding 2% cationic starch was between 89% and 97% and correlates well with the literature that reports an increase of tear-index up to 89% after adding 2% cationic starch (Ghasemian et al., 2012). Previous reports

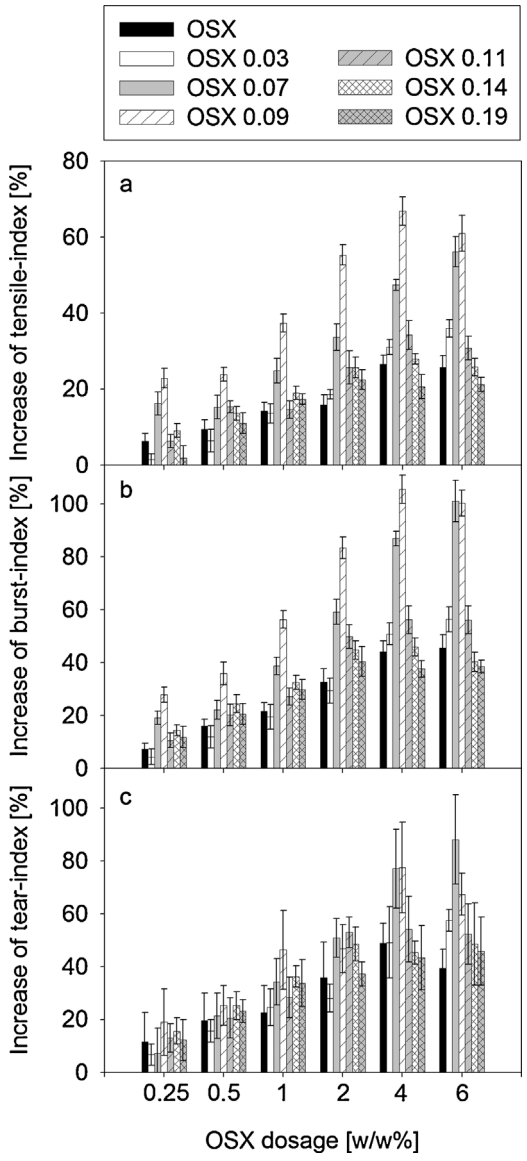

Fig. 3. Influence of OSX addition with doses between 0.25% and 6% and different DS values on the tensile- (a), burst- (b) and tear-indices (c) of hand sheets.

indicate that the increases in the tensile- and burst-indices are higher than the increase in the tear-index after adding xylan (Bai et al., 2012; Ramirez et al., 2008). The different effects of cationic starch and xylan on the tear-index might be rationalized by the effects of the different molecular structures of starch and xylan on the destruction mechanism during the tear measurement. The main phenomenon observed in tear tests is the drawing of the fibers out of the paper structure and the breaking of fibers (Fellers, 2009). According to Glittenberg (1993), the amylose and amylopectin contents in the starch, as well the molecular-structure of the amylose and amylopectin polymers, may influence the retention and the improvement of the mechanical paper properties. In general, the M_w of the amylose fraction (10^4–10^5) in most starches is smaller than the M_w of amylopectin (10^6–10^8) (Glittenberg, 1993; Jane, Maningat, & Wongsagonsup, 2010, chap. 10; Yoo & Jane, 2002). Therefore, starch contains amylose in addition to highly branched amylopectin, while xylan contains only linear chains. The better tear-index generated by adding cationic starch might be caused by the branched amylopectin's superior ability to prevent the fibers from being drawn out of the paper network.

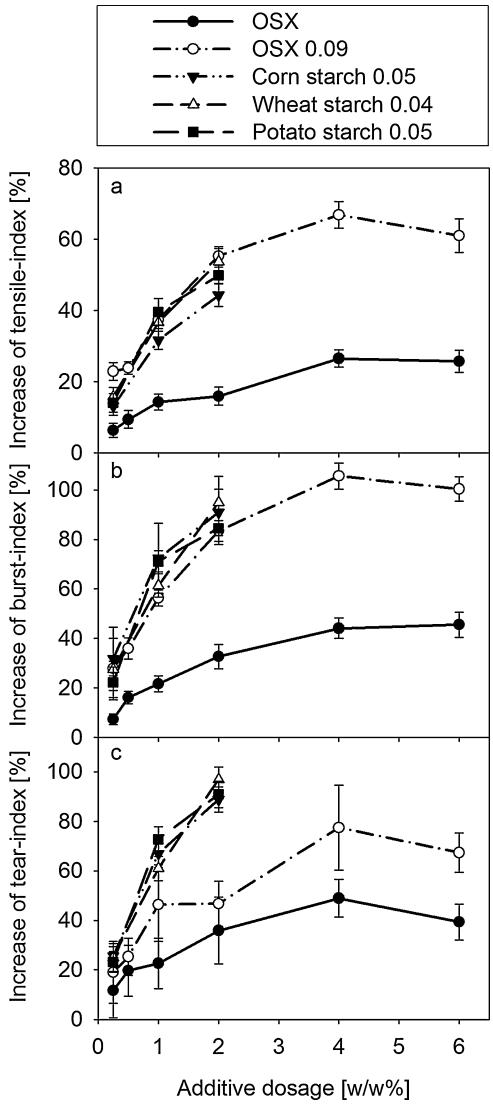

Fig. 4. Comparison of the tensile- (a), burst- (b) and tear-indices (c) after adding xylan (0.25–6%, w/w) or starch (0.25–2%, w/w) to the hand sheets.

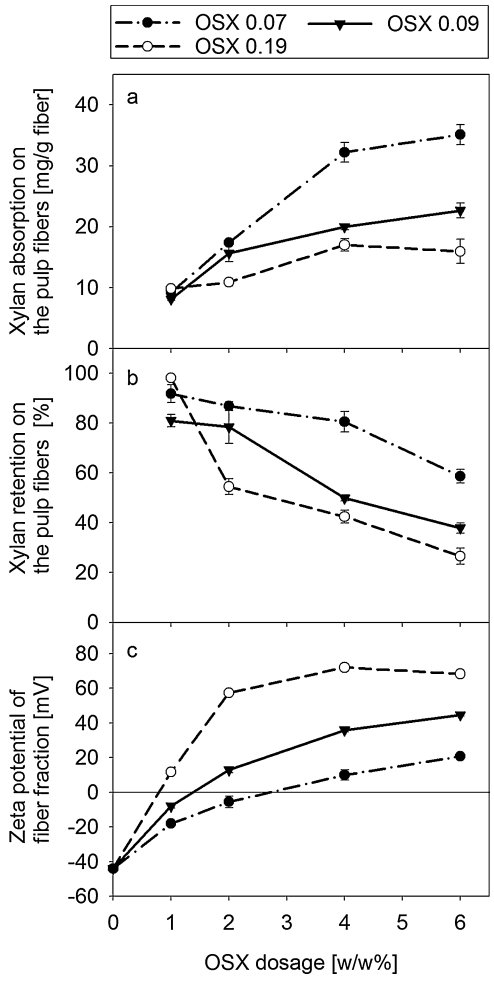

Fig. 5. Influences of different DS and OSX doses on the xylan absorption on the fibers (a), xylan self-retention (b) and the zeta potential of the fiber fraction (c).

3.4. Absorption of cationic xylan on pulp fibers

The absorption of an additive on the pulp fibers is a basic requirement to improve the mechanical paper properties (Pelton, 2004; Silva et al., 2011; Zhang et al., 2001). OSX 0.07, OSX 0.09 and OSX 0.19 were chosen to study the absorption onto the fibers. OSX 0.07 and OSX 0.09 were selected because they induced the largest strength increases and exhibited a medium charge density (219 or 391 μequiv./g). Furthermore, the OSX 0.19 sample with the highest charge density (729 μequiv./g) was used for comparison. The absorption and retention behaviors of the three cationic xylans in additive dosages between 1% and 6% are depicted in Fig. 5a and b. In addition, the zeta potential of the fibers was determined for the absorption experiments (Fig. 5c).

The amount of absorbed cationic xylan on the pulp fibers was calculated per gram of pulp fibers (mg/g) (Fig. 5a). In general, the absorption behavior and the strength properties (Fig. 3) display the same tendencies relative to the additive dose. Therefore, by increasing the xylan dosage, the absorption is also continuously increased; the highest values for all three cationic OSX were measured at xylan doses from 4% to 6%. The applied xylan dose displaying the best absorption was always determined for OSX 0.07. The absorption values reached with the doses of 4 and 6% were 32 or 35 mg/g, respectively. OSX 0.09 likewise displayed its maximum absorption between 4% and 6%, however only between 20 and 23 mg/g OSX 0.09 was absorbed on the fibers. Although the amount absorbed on the fibers was 12 mg/g lower for OSX 0.09, the effect exerted on the mechanical paper properties was nearly identical at the 6% dose (see Fig. 3). Therefore, the absorbed amount of cationic xylan enhanced the paper strength. Additionally, using the optimal amount of cationic side groups seems to affect the strength improvement. Smaller amounts of absorbed OSX 0.09 might be compensated by the more beneficial charge density. The OSX 0.09 had a 5% lower ash content then OSX 0.07, possibly accounting for the good strength improvements observed despite the lower absorption. However, when considering the differences in strength and ash values, it is unlikely that the lower ash content solely accounts for the strength difference. The number of cationic groups on the xylan is the major influence on paper strength. The highest charged sample (OSX 0.19) displayed in the lowest absorption: between 17 and 16 mg/g for a dose between 4% and 6%. The strength improvement caused by adding OSX 0.5:1 was only half as large as the improvements displayed by the other two OSX samples (see Fig. 4). Therefore, the charge density (788 μequiv./g) was too high to positively affect the absorption and strength. The samples with a medium cationic charge displayed absorption behavior between 219 (OSX 0.07) and 391 μequiv./g (OSX 0.09), which were the best results. This result validates the strength increases presented in Fig. 3. The absorption experiments

revealed that the different EPTA:AXU ratios, as well as the resulting DS and cationic charge, influenced the amount of xylan remaining on the pulp fibers. An excessively high cationization translated to a lower absorption of cationic xylan. This effect was also observed in the literature for cationic potato starch. The amount of absorbed starch was higher when the DS was very low (DS 0.005–25 mg/g) compared to starches with a higher DS (DS 0.05–10 mg/g) (Wagberg & Kolar, 1996). However, it was also reported that high charged cationic birch xylan (740 μequiv./g and DS 0.2) was absorbed in high amounts (28.4 mg/g) on pulp fibers when compared to less charged cationic xylans (Köhnke, Brelid, & Westman, 2009). These data are surprising and might be due to the different birch and oat spelt xylan structures, or solubilities. Differences of pulp fibers might be also of importance. The general theory for the absorption of charged polymer on fibers assumes that the polymers with lower charges may be absorbed on the fibers in higher amounts. Polymers with a high cationic charge build a close film around the cellulose fiber, but the more neutral polymers form loops and tails that do not surround the fiber surface; these phenomena lead to a higher absorption of lower charged polymers onto cellulose fibers (Hubbe, 2006; Salmi, Osterberg, Stenius, & Laine, 2007) and are consistent with the findings of this study.

Fig. 5b depicts the retention of the three cationic xylan samples by the paper as a percentage of the applied xylan. A low additive retention leads to more water cycle contamination and less efficiency during paper production. Therefore, a high retention is desirable for paper-making. At the lowest additive dose (1%), retention rates between 81% and 98% were measured for all three cationic xylans. With increasing doses, the retention decreased continuously. The best performance at a 4% dose was obtained for OSX 0.15:1 with 81% retention. Further increases up to 6% in xylan dose precipitously decreased the retention of OSX 0.07 (59%). The second best retention was observed for OSX 0.09. At a 2% dose, the retention remained above 78%. The sharpest retention decrease was revealed for OSX 0.19. The retention of a 2% dose was only 55%. In general, the retention of every OSX sample was between 81% and 98% when the dosage was near 1%. The literature reports similar values for cationic starch. Retention rates between 81% and 98% were obtained with doses between 0.7% and 1%, (Glittenberg, 1993).

Fig. 5c depicts the zeta potential of the fiber fraction. The surface charges of pulp suspensions influence the aggregation of and absorption on paper additives (Bhardwaj, Hoang, & Nguyen, 2007; Cadena, Garcia, Vidal, & Torres, 2009; Hubbe, Nanko, & McNeal, 2009). Pulp fibers carry a slightly negative charge because carboxylate groups are introduced during the pulping and bleaching processes (Potthast et al., 2003; Schleicher & Lang, 1994). Therefore, the original eucalyptus kraft pulp displayed a negative zeta potential (−44 mV). Depending on the charge density of the added cationic OSX the zeta potential increased slower or faster. For the sample with the lowest cationic charge (OSX 0.07), the zeta potential of the fibers increased steadily with the xylan dose; the saturation of the fibers was not observed. The zeta potential measured after adding OSX 0.09 was cationic (13 mV) for a 2% dose. At a 6% (maximum) dose of OSX 0.09, the maximum zeta potential (45 mV) was obtained. The steady increase in the zeta potential curve revealed that the fibers were not yet saturated with OSX 0.09. OSX 0.19 had the highest charge density and the strongest effect on the zeta potential. At a 1% dose, a positive zeta potential was obtained. The charge maximum (72 mV) was reached at 4% and did not increase further at the 6% dose. This plateau in the zeta potential indicated that the paper was overcharged and the fibers were saturated with OSX 0.19. The zeta potential data agreed with the retention behavior and literature reports. Various studies reported a maximum retention of paper additives occurred at a zeta potential close to zero (Bhardwaj, Kumar, & Bajpai, 2005; Hubbe, Nanko, & McNeal, 2009; Salmi et al., 2007). For all products, high retention values (Fig. 5b) (80%) were achieved at doses displaying zeta potentials below 15 mV. Therefore, the zeta potential explained why different doses (4% OSX 0.07, 2% OSX 0.09 and 1% OSX 0.19) displayed additive retentions above 80%.

4. Conclusions

Cationic OSX addition significantly increased the mechanical properties of paper, whereas cationic WX had only a small influence due to impurities and a different structure. Therefore, only OSX was comprehensively tested to determine the optimal functionalization degree and dose. The optimal EPTA:AXU ratio was between 0.15:1 and 0.2:1. The doses leading to the highest strength increase were observed with OSX 0.07 at 6% and OSX 0.09 at 4%. OSX 0.09 increased the tensile index by 66%, the tear-index by 77% and the burst-index by 105% under optimal conditions. Under optimal conditions, the medium charged xylans absorbed in concentrations of 24 mg/g (OSX 0.09) and 32 mg/g (OSX 0.07). These data validated the strength improvement measurements: the addition of excessively charged xylans generate lower increases in strength. Compared to cationic starch, OSX 0.09 caused similar increases in tensile- and burst-indices. However, adding OSX 0.09 enhanced the tear-index only half as much as adding cationic starch in similar amounts. In conclusion, the amount of absorbed xylan and cationic side groups, as well as the molar mass, structure and purity of the xylan, influenced the enhancements of paper strength. The differences between cationic starch and cationic OSX regarding the tear strength improvements were most likely observed because the OSX had a lower molar mass. Crosslinking the xylan chains might furnish an additional improvement to the mechanical paper properties. The price of starch is notably low, making the use of crosslinked xylans economically difficult. However, the use of xylan as paper additive would not compete with the food market and huge quantities of unused xylan are potentially available for this application.

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