Carbohydrate Polymers 102 (2014) 627–635

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

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

Alexander L. Deutschle[a], Katrin Römhild[b], Frank Meister[b], Ron Janzon[c], Christiane Riegert[c], Bodo Saake[c,*]

[a] Johann Heinrich von Thünen-Institut (TI), Institute of Wood Research, Leuschnerstr. 91b, 21031 Hamburg, Germany
[b] Thüringisches Institut für Textil-und Kunststoff-Forschung e.V. (TITK), Breitscheidstr. 97, D-07407 Rudolstadt, Germany
[c] University of Hamburg, Department of Wood Science and Chemical Wood Technology, Leuschnerstr. 91b, 21031 Hamburg, Germany

ARTICLE INFO

Article history:
Received 1 August 2013
Received in revised form 3 December 2013
Accepted 5 December 2013
Available online 14 December 2013

Keywords:
Oat spelt xylan
Wheat xylan
Paper strength additive
Cationic polymers
Xylan absorption

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

* Corresponding author. Tel.: +49 040 73962510; fax: +49 040 73962599.
E-mail address: bodo.saake@ti.bund.de (B. Saake).

0144-8617/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.carbpol.2013.12.016

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,