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Periodate oxidation of xylan-based hemicelluloses and its effect on their thermal properties

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ABSTRACT

Hemicellulose from pulp mill process water and crop residuals from food production often end up in waste streams or burnt for energy contribution. These waste products contain valuable biopolymers but lack many attributes needed for use in applications such as food and medical or consumer products. This study reports on an investigation of the periodate oxidation of hardwood xylan and arabinoxylan (AX) from wheat bran to produce materials with new functionalities. The study explores how to control the oxidation degree and describes structural differences between the two xylan-based polymers. For the xylan samples, the oxidation resulted in a lowering of the glass transition temperature (T_g), indicating a more flexible chain due to ring-opening of the xylan anhydro-sugar units. For the AX samples, the arabinose side-groups were instead oxidized, hindering oxidation on part of the xylose units, which resulted in a crosslinked network with an unchanged T_g but reduced intrinsic viscosity.

1. Introduction

Hemicelluloses constitute about one third of all biomass on Earth. Despite this high volume, knowledge, and consequently use, of the biopolymers is low compared to cellulose, for example. Hemicelluloses are defined as non-starch polysaccharides found in plant cell walls connected to cellulose (Ebringerová, Hromádková, & Heinze, 2005). There are many varieties of hemicellulose in nature, depending on origin, and there are in general four classes of structurally different cell-wall polysaccharides; xylan, mannans, β-glucans and xyloglucans (Ebringerová et al., 2005).

Xylan is the main hemicellulose in hardwood specimens and varieties of xylan-based hemicelluloses can also be found in cereals, grasses and other annual and perennial plants. The xylan-based polymers found in cereals and grasses are commonly referred to as arabinoxylan (AX). Xylan polymers are built up by a linear chain of xylose units linked together through a 1,4-β-linkage. Uronic or ferulic acids and/or arabinofuranose side-groups can be substituted for parts of the polymers.

AX has a backbone of xylan with arabinose side groups substituted for part of the xylose groups. The substitution patterns of arabinose groups vary between different specimens but substitution is often through either the C2 or C3 position of xylan or both through beta linkage (zydorczyk, 2009). The number of arabinose groups can vary depending on species, isolation method, polymer length and chemical reactions such as degradation. Studies have also shown that in AX from wheat the arabinose groups are ordered in blocks on the backbone while in AX from barley the arabinose side groups are more evenly spread out over the backbone (Hoffmann, Kamerling, & Vliegenthart, 1992).

Hemicelluloses, like other polysaccharides, are considered as less-flexible polymers due to the rigid carbohydrate rings and inter- and intra-chain hydrogen bonding of hydroxyl groups. By introducing flexibility into the polymer, new functionalities can be achieved due to the changed physio-chemical properties of the polymers. Periodate oxidation is one way of creating “hinges” in a polysaccharide backbone and has for a long time been used as a routine method for structure determination of complex carbohydrate structures (Kristiansen, Potthast, & Christensen, 2010). For the periodate oxidation reaction, the periodate ion (IO_4^-) cleaves the carbon–carbon bond in the vicinal, leading to the formation of a dialdehyde. At the same time, several side-reactions occur, competing with the periodate oxidation. When the carbohydrate is opened into its dialdehyde form, intramolecular hemiacetal formation can occur between the dialdehyde groups and hydroxyl groups of neighboring unoxidized anhydrosugar units (Larsen & Painter, 1969). This will hinder oxidation on the neighboring carbohydrate. In addition, depolymerization of the polymer occurs via two different routes. A peeling reaction starts from the reducing-end groups, caused by over-oxidation (Vold & Christensen, 2005) or owing to

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random attack by hydroxyl radicals formed by the spontaneous decomposition of periodate ions in the solution (Scott & Page Thomas, 1976).

Dialdehyde cellulose, which has been known for a long time, contains two aldehyde groups and is prepared from periodate oxidation, in which almost all the glucose units are opened. In recent years, dialdehyde polysaccharides have been obtained through periodate oxidation on cellulose (Azzam, Galliot, Putaux, Heux, & Jean, 2015; Kim, Kuga, Wada, Okano, & Kondo, 2001; Larsson, Berglund, & Wågberg, 2014; Siller et al., 2015), alginate (Gomez, Rinaudo, & Villar, 2007; Nygård Vold, Kristiansen, & Christensen, 2006; Smidsrød & Painter, 1973), chitosan (Vold & Christensen, 2005), starch (Fiedorowicz & Para, 2006; Veelaert, Wit, Gotlieb, & Verhé, 1997; Yu, Xiao, Tong, Chen, & Liu, 2007), mannans (Ďurana, Lacík, Paulovicová, & Bystrický, 2006) and xylans (Chemin et al., 2016; Dervilly-Pinel, Tran, & Saulnier, 2004; Revanappa, Nandini, & Salimath, 2010). Possible application areas suggested for periodate oxidized polysaccharides in the literature are crosslinking hyaluronic acid gels for biomedical applications (Khunmanee, Jeong, & Park, 2017), tissue engineering (Bouhadir et al., 2001), drug delivery, flocculating agents or reactive chemical anchors for further reactions (Fredon et al., 2002). High-density films made from oxidized fibrillated or dissolved cellulose, as well as other types of polysaccharides, are known to act as good oxygen barriers (Aulin, Gällstedt, & Lindström, 2010; Fukuzumi et al., 2011; Gröndahl, Eriksson, & Gatenholm, 2004; Larsson et al., 2014). These polysaccharides would be possible candidates for the replacement of petroleum-based plastics in, for example, various packaging applications.

This study highlights the reaction conditions for periodate oxidation of xylan and arabinoxylan and discuss how the oxidation of the polymers affects their thermal properties. The arabinoxylan used was isolated from wheat bran, it has a high amount of substituted arabinose side-groups and the contribution of those side groups were studied. The hypothesis for the study steams from the fact that many synthetic polymers with a low T_g shows high flexibility and processability. Here, we investigate the potential lowering of T_g for xylan and arabinoxylan via oxidation route yielding an open more flexible xylan chain for xylan and a xylan backbone with flexible open arabinose units.

2. Experimental

2.1. Materials

Beechwood xylan was provided by Sigma-Aldrich. Proton NMR analysis of the material showed 13% uronic acids in the sample, which was evaluated in an earlier study (Börjesson & Westman, 2016). Wheat bran was kindly provided by Lantmännen, Sweden. The chemicals used in the alkaline extraction were provided by Sigma-Aldrich, unless otherwise stated. The sodium (meta)periodate was provided by Riedel de Haen AG. Dialysis membrane (Spectra/Por 3) with a molecular weight cut-off of 3.5 kDa was purchased from Spectrum Labs.

2.2. Isolation of arabinoxylan

Arabinoxylan was isolated from wheat bran using an alkaline extraction process described in earlier work (Börjesson et al., 2018). As a pre-hydrolysis, 500 g flakes of wheat bran were stirred in 10 l of 0.05 M hydrochloric acid (HCl) at room temperature during one night. The wheat bran flakes were then filtrated and the solid residue mixed with 2 l deionized water and 75 g sodium chlorite. The delignification occurred at 80 °C for 3 h and at a pH of 3.1, adjusted with sodium hydroxide (NaOH). After delignification the sample was filtrated and the solid residue was dispersed in 1 M NaOH-solution (5 l) containing 50 g sodium thiosulfate as reducing agent. The alkaline extraction was performed overnight at room temperature. The extraction was neutralized by the addition of HCl with the cellulose precipitate and the hemicellulose remaining in the aqueous solution. The precipitated cellulose was separated from the hemicellulose fraction through centrifugation at 4300 rpm for 10 min (Heraeus Megafuge 40, Thermo Scientific). The hemicellulose fraction obtained after isolation contained high amounts of glucose (approximately 18% of the carbohydrate content), which originated from starch and β-glucan (Comino, Shelat, Collins, Lahnstein, & Gidley, 2013). The glucose-starch was removed from the arabinoxylan by the addition of 3 ml α-amylase (Termamyl 120) to a 0.5 wt% AX/water solution, heated at 60 °C for 15 h, followed by dialysis against deionized water.

2.3. Periodate oxidation of hemicelluloses

Xylan and AX hemicelluloses were oxidized following a method similar to the one described by Amer and co-workers (mer et al., 2016). 25 ml of a $NaIO_4$ solution with varying amounts (between 0.125 and 0.625 mol eq.) of $NaIO_4$ per mole of anhydroxylose unit (AXU) were added to a 75 ml water suspension consisting of approximately 2 g hemicellulose. The molar mass of the AXU used in calculation of moles was 132.1 g/mol. The reaction was protected from light, under stirring and at ambient conditions. The progress of the reaction was followed with ultraviolet spectroscopy by studying the absorption band at $\lambda = 290$ nm corresponding to the concentration of IO_4^-. A linear standard curve for the periodate solution at $\lambda = 290$ nm was obtained using concentrations of $NaIO_4$ between 0.1 to 5 mM, in accordance with Maekawa and co-workers (Maekawa, Kosaki, & Koshijima, 1986). After reaction, the solution was purified by dialysis against deionized water.

2.4. Characterization

The progress of the oxidation reaction was followed using a Cary 60 UV–vis ultraviolet spectrometer (Agilent Technologies). The oxidized hemicellulose samples were diluted to be in the range of the linear standard curve (0.1–5 mM). The diluted samples were analyzed in quartz cuvettes between 800 and 200 nm with a scanning rate of 300 nm/min.

The aldehyde content in the different samples was calculated from the final consumption of periodate (mmol) measured by UV–vis, divided by the weight of the hemicellulose (g) used in the reaction from start. Since one mole of periodate is assumed to give two moles of aldehyde groups, the consumption of periodate was multiplied by two (see Eq. (1)).

$$Aldehyde\ content\left[\frac{mmol}{g}\right] = \frac{2 \times consumed\ amount\ of\ NaIO_4\ [mmol]}{m_{Hemicellulose}\ [g]} \quad (1)$$

The characteristic chemical-bond presents in the oxidized samples were detected by using FTIR spectroscopy. The FTIR were recorded on a Perkin Elmer Frontier FT-IR Spectrometer equipped with an attenuated total reflection (ATR) device. Dried hemicellulose samples were placed on the ATR crystal. All spectra were averaged from 16 scans from 4000 to 400 cm^{-1}. The FTIR spectra were baseline corrected and normalized according to the largest absorption band of each spectra using the in-built functions in the Spectrum 10 software (Perkin Elmer, version 10.4.3).

The neutral carbohydrate composition of the samples was analyzed in three replicates on hydrolyzed hemicellulose samples by high performance anion exchange chromatography with pulsed amperometric detection (HPAEC-PAD), using an ion chromatography system ICS 3000 (Dionex) equipped with a CarboPac PA1 (4 × 250 mm) analytical column, a gradient pump, isocratic post column pump, column oven and autosampler. The different sugars detected with the available system were arabinose (Ara), galactose (Gal), glucose (Glc), xylose (Xyl), and mannose (Man). Prior to analysis the samples were hydrolyzed with a 72% sulfuric acid according to Theander and Westerlund and diluted to a concentration of 200 mg/l (Theander & Westerlund,