



Carboxymethylated-, hydroxypropylsulfonated- and quaternized xylan derivative films



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ARTICLE INFO

Article history:

Received 17 March 2014

Received in revised form 13 April 2014

Accepted 16 April 2014

Available online 26 April 2014

Keywords:

Xylan

Films

Properties

Molar masses

AFM

ABSTRACT

Under alkaline/water conditions carboxymethyl, 2-hydroxypropylsulfonate and trimethylammonium-2-hydroxypropyl groups were introduced into xylan in one step with the goal to prepare film specimens. The materials were characterized by NMR, SEC-MALS, TG/DTG/DTA, AFM and mechanical testing. The properties of triple, double and mono-substituted materials were compared. The numerical molar masses of the specimens were from 12.3 to 17.6 kg/mol with M_w/M_n from 1.27 to 1.34. The elastic modulus values are decreasing in order: xylan (X; 7354 MPa) > carboxymethyl xylan (CX; 6090 MPa) > 2-hydroxypropylsulfonate xylan (SX; 6000 MPa) > carboxymethyl/2-hydroxypropylsulfonate xylan (CSX; 4490 MPa) > quaternized xylan (QX; 3600 MPa) > carboxymethyl/quaternary/2-hydroxypropylsulfonate xylan (CQSX; 3380 MPa) > carboxymethyl/quaternary xylan (CQX; 2805 MPa). The onset temperatures of SX (214 °C), CQSX (212 °C), QSX (211 °C) and CQX (207 °C) were higher than for X (205 °C). The roughness values of the film surfaces (3.634 – 18.667 nm) are higher on top than on the bottom of the specimen.

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1. Introduction

Xylan is an important polysaccharide used for composite preparation, film and package applications (Hansen & Plackett, 2008; Köhnke, Lin, Elder, Theliander, & Ragauskas, 2012; Saxena, Elder, Kenvin, & Ragauskas, 2010; Saxena, Elder, & Ragauskas, 2011; Šimkovic, 2013). Carboxymethyl and quaternary xylan (CQX) was recently studied for preparation of an amphoteric polysaccharide derivative of water soluble xylan from bamboo in two steps using microwave (Peng, Ren, Zhong, & Sun, 2012). Carboxymethyl xylan (CX) was also prepared from birch kraft pulp after extraction of xylan and subsequent carboxymethylation (Alekhina, Mikkonen, Alén, Tenkanen, & Sixta, 2014). The reaction has been previously performed, but fully substituted CX was not prepared. By the repeated “slurry” method $DS_C = 1.90$ was reported without considering the molar mass of the produced derivatives (Petzold-Wecke,

Schwikal, Daus, & Heinze, 2014). Carboxymethyl xylan (CX) was also prepared from birch kraft pulp (Alekhina et al., 2014).

Because our beech wood xylan was isolated by NaOH extraction and is only partially soluble in water we used conventional heating instead of microwave to prevent the dramatic molar mass degradation. From our previous studies on the preparation of trimethylammonium-2-hydroxypropyl xylan (QX), 2-hydroxypropylsulfonate (SX) and trimethylammonium-2-hydroxypropyl xylan sulfate (QXS) we have learned that the numerical molar masses (M_n) of the produced material were larger than the water-soluble part of the used xylan (Šimkovic, Gedeon, Uhliariková, Mendichi, & Kirschnerová, 2011a, 2011b; Šimkovic, Tracz, Kelnar, Uhliariková, & Mendichi, 2014). In this work we have used a method in which several ion-exchanging substituents were introduced in one step and the degree of substitution (DS) values were compared with values when single substituent was introduced under analogous conditions. The mechanical properties of the prepared films were studied and compared with data in the literature. The goal was to understand the relation between the chemical structure of the polysaccharide, the type of substituent, molar mass and water solubility together with the effect of

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chemical modification on thermal stability, optical and mechanical properties of the films.

2. Experimental

2.1. Materials

Xylan (X) was extracted from beech sawdust holocellulose with 10% NaOH as previously described for hornbeam wood (Ebringerová, Kramár, & Domanský, 1969). It was characterized as described before (Šimković et al., 2011a, 2011b, 2014). All the chemicals used were of analytical grade and were used without further purification.

CX was prepared by mixing X (1.654 g; 10 mmol) with water (18 ml; 1 mol), containing NaOH (3.2 g, 80 mmol). Subsequently 4.7543 g of ClCH₂COONa (40 mmol; Alfa Aesar) was added and stirred (500 RPM) at 60 °C in a closed container for two hours. The reaction was stopped by dilution, the pH adjusted to 8.0 with HCl, and dialyzed using 10–12 kDa molar mass cut-off dialysis tubing (SERVA # 44126). After preconcentration on a vacuum evaporator (35 °C; 3.3–4 kPa) the solution was freeze-dried [CX, 1.9277 g; C, 34.53; H, 5.34; DS_C = 0.63 (determined with the ¹H-NMR spectroscopy by integration of all xylose anomeric signals and calculated as a ratio of carboxymethylated xylose anomeric signal to all the xylose anomeric signals); yield = (amount of CX obtained/theoretical yield at determined DS) × 100 = 85%].

For preparation of carboxymethyl/trimethylammonium-2-hydroxypropyl xylan (CQX) 1.654 g (10 mmol) of X was mixed with water (16.21 ml; 1 mol in total) containing 6.4 g NaOH (160 mmol). Subsequently 4.7543 g of ClCH₂COONa (40 mmol) and 8.94 ml of glycidyltrimethylammonium chloride (GTMAC, 60% solution, Aldrich; 40 mmol) were added and stirred as above for two hours. The solution was adjusted to pH 10.0, dialyzed and worked up as above [CQX; 2.1384 g; C, 42.49; H, 7.03; N, 2.32; DS_Q = (nitrogen content/nitrogen content of fully substituted derivative) × DS of fully substituted derivative [(2 × amount of xylose units not substituted with 4-O-methyl-D-glucuronate unit) + (3 × amount of xylose units substituted with 4-O-methyl-D-glucuronate unit)] = (2 × 0.86) + (3 × 0.14) = 2.14] = 0.35; DS_C = DS_{NMR} – DS_Q = 0.60 – 0.35 = 0.25; yield = 90%].

The carboxymethyl/2-hydroxypropylsulfonate xylan (CSX) was prepared by mixing X (1.654 g; 10 mmol) with water (18 ml; 1 mol) containing NaOH (6.4 g; 160 mmol) and subsequent addition of 8.5836 g of 3-chloro-2-hydroxy-1-propanesulfonic acid, sodium salt (CHPS, 40 mmol; Aldrich) and 4.7543 g of ClCH₂COONa (40 mmol). The sample was stirred (500 RPM) at 60 °C for two hours and worked up as above [CSX, 1.9140 g; S, 1.12; C, 36.97; H, 5.34; DS_S = (sulphur content/sulphur content of fully substituted derivative) × DS of fully substituted derivative = 0.08; DS_C = DS_{NMR} – DS_S = 0.55 – 0.08 = 0.47; yield = 52%].

The carboxymethyl/2-hydroxypropylsulfonate/trimethylammonium-2-hydroxypropyl xylan (CSQX) was prepared by mixing X (1.654 g; 10 mmol) with water (16.21 ml; 1 mol in total) containing NaOH (6.4 g; 160 mmol) and subsequent addition of 4.7543 g of ClCH₂COONa (40 mmol), 8.5836 g of CHPS (40 mmol) and 8.94 ml of GTMAC (40 mmol). The reaction was run for two hours at 60 °C and worked up as above [CSQX; 1.6769 g; N, 2.25; C, 41.01; H, 6.95; S, 0.72; DS_Q = 0.32; DS_S = 0.05; DS_{NMR} = 0.66; DS_C = DS_{NMR} – DS_Q – DS_{SA} = 0.66 – 0.32 – 0.05 = 0.29; yield = 37%].

For comparison an analogous experiment was performed at the ratio of X/NaOH/CHPS/H₂O = 10/80/40/1000 with a 2 h treatment and worked up as above for the preparation of SX (1.7994 g; C, 36.71; H, 6.11; S, 2.33; DS_S = 0.37; DS_{NMR} = 0.32; yield = 80%). Similarly, QSX (1.5643 g; N, 1.62; C, 41.05; H, 6.68; S, 1.85; DS_Q = 0.23; DS_S = 0.13; DS_{NMR} = 0.39; yield = 53%) was obtained by the reaction

of X/NaOH/GTMAC/CHPS/H₂O = 10/160/40/40/1000 for 2 h, with the treatment and work up as above. QX was prepared at X/NaOH/GTMAC/H₂O = 10/80/40/1000, a two hour treatment and worked up as above (1.1325 g; N, 2.08; C, 40.20; H, 6.72; DS_Q = 0.25; DS_{NMR} = 0.46; yield = 47%). The SX and QSX were also prepared previously (Šimković et al., 2011a), but the NMR data of these derivatives were not completely assigned and are also listed in Table 1.

2.2. Analytical methods

Solution NMR measurements were performed as described previously (Šimković et al., 2011a). The elemental composition of specimens was performed using a FLASH 2000 Organic elemental analyzer (Thermo Fisher Scientific; furnace temperature: 950 °C; PTFE column, 6 o.d./5 mm i.d. × 2 m; 65 °C; helium as carrier and reference gas at 140 and 100 ml/min; oxygen flow: 250 ml/min; 720 s run time; 12 s sampling delay; 5 s injection end).

SEC-MALS characterization was performed using 0.1 M acetate buffer at pH 4.5 as SEC mobile phase (two TSK gel columns; G4000 and G3000; Tosoh Bioscience; at 35 °C; flow rate: 0.8 mL/min; dn/dc = 0.146 g/ml; sample concentration: 3 mg/ml).

AFM imaging was performed using a Digital Instruments Dimension 3100 Series Scanning Probe Microscope (SPM) equipped with a NanoScope IIIa SPM Controller. The top and the bottom surfaces of the films were imaged at a scan size of 5 μm in tapping mode using an etched silicon probe (TESP) at a scan rate of 1.969 Hz. Five images were obtained for each side of individual samples, which were then processed prior to analysis. Raw images were flattened so as to remove the any vertical offset between the scan lines arising out of possible vertical scanner drift, image bow and skips. These were then subject the 'XY PlaneFit' command to remove any tilt or bow from the images before the roughness and section analyses were performed. Analysis of the captured images involved calculating the root mean square (RMS) roughness values of both sides and performing a Section analysis by cutting cross-sectional lines between opposite corners of the images. The RMS roughness value is obtained as the standard deviation of the Z (height) values within a given area, using the following equation:

$$\text{RMS} = \left(\frac{\sum_{i=1}^N (Z_i - Z_{\text{ave}})^2}{N} \right)^{(1/2)}$$

where Z_{ave} refers to the average Z value within the given area, Z_i is the current Z value, and N is the number of points within a given area or section analysis profile. The roughness values are reported as averages for the five images taken. Section analysis provides with the depth, height, width and the angular measurements across an indicated section. Horizontal and vertical distance, the mean roughness and the maximum difference in height on the surface relative to the mean plane (R_{mzx}) are reported as obtained between the chosen cursor points, ~2.12 μm apart. All other methods were described previously (Šimković et al., 2014).

2.3. Film preparation

All the films were prepared by the casting method using plastic Petri dishes (7 cm in diameter) and one gram of lyophilized sample dissolved in 50 ml of water and stirred overnight at 1250 RPM.

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