



Quaternized and sulfated xylan derivative films



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ABSTRACT

Xylan quaternized sulfate films were prepared from beech xylan (X) and compared with fully sulfated xylan films (XS). When quaternized xylan (QX) was prepared in the first step ($DS_Q = 0.55$), than by sulfation of QX in the second step the fully substituted ampholytic derivative (QXS; $DS_Q = 0.33$; $DS_S = 1.67$) could be obtained. By sulfation in first step, xylan sulphate (SX, $DS_S = 0.70$) was obtained and by subsequent quaternization, SXQ film with $DS_Q = 0.55$ and $DS_S = 0.33$ which contained partially unsubstituted hydroxyls. The molar masses (M_n) of the film's soluble parts were increasing in order $X < SX < SXQ < QX < XS < QXS$. In all films there were some insoluble particles present as determined by the amount of recovered masses by SEC-MALS. The materials were further characterized by AFM, XRD, TG/DTG/DTA, NMR and mechanical testing. QXS and SXQ could form mechanically more stable films than XS specimens.

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1. Introduction

Composites and especially films from all-polysaccharide composites (Šimkovic, 2013) are increasing its importance due to ecological aspects and interesting properties. Also xylan-containing films were intensively studied (Deutschmann & Dekker, 2012; Grondahl, Erisson & Gatenholm, 2004; Hansen & Plackett, 2008; Mikkonen et al., 2012; Peng, Ren, Zhang & Sun, 2011; Šimkovic, Gedeon, Uhliariková, Mendichi & Kirschnerová, 2011a,b; Šimkovic, 2008; Zhang & Whistler, 2004). Their applications are dependent upon their properties. Partially water soluble films could be used for covering the surfaces of food, pharmacological and other products to prevent drying or oxidative changes. Their mechanical and optical properties are dependent upon molar mass, presence of ion-exchanging groups and water solubility.

The use of scanning electron microscopy (SEM) in previous studies allowed us to make conclusions about the homogeneity of the film surface as well as on the break. When broken the film is mechanically destroyed its structure could be observed on the fracture from inside (Šimkovic et al., 2011a,b). With the use of atom force microscopy (AFM) besides better enlargement also the third dimension of the surface could be observed at the nanometre scale. We also used SEC-MALS, XRD, mechanical tester, solution and solid state NMR spectroscopy and thermal analysis (TG/DTG/DTA) to

characterize the samples. This data made it possible to understand the relation between chemical structure, type of substituent, molar mass and water solubility together with the effect of chemical modification on homogeneity of the surface, tensile strength of the films and thermal properties of the material.

2. Experimental

2.1. Materials

Xylan (X) was extracted from beech sawdust holocellulose with 10% NaOH analogous to that described for hornbeam wood (Ebringerova et al., 1969). According to ¹H NMR anomeric signals integration of the soluble part at 60 °C in 100 atom% D₂O (ARMAR Chemicals), the sample contained 16.67% of 4-O-methyl-D-glucuronic units and 83.33% of xylose. The sonicated fraction (132 kHz, 129 W, 18 × 10 min at 50 °C, WX) had $M_n = 3.8$ kg/mol and $D = 2.0$ according to SEC-MALS analysis (see Section 2.2) 64.2% of sample mass was recovered. Sulphur trioxide pyridine complex (Py-SO₃, Aldrich) and all other chemicals used were of commercial grade and were not further purified.

Quaternized xylan (QX) was prepared by mixing X (1.654 g; 10 mmol) with glycidyltrimethylammonium chloride (GTMAC; 4.47 ml, 20 mmol; 60% solution) and water (17 ml; 1 mol in total), containing NaOH (1.6 g, 20 mmol). After stirring (500 RPM) at 60 °C for seven hours the reaction was stopped by dilution and adjusted to pH 5.0 with HCl and dialyzed using 10–12 kDa molar mass cut-off dialysis tubing (SERVA # 44126). After preconcentration

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on vacuum evaporator (35 °C; 3.3–4 kPa) the solution was cast on Petri dish and dried at room temperature (RT) to prepare film (QX, 1.8574 g; N, 1.93; C, 40.49; H, 6.94; $DS_Q = [\text{nitrogen content (\%)/nitrogen content of fully substituted anhydroxylose (\%)}] \times 2 = 0.55$; yield = [theoretical yield at obtained DS/amount of X used] $\times 100 = 69\%$).

In the second step QX (0.9287 g; 5 mmol) was mixed with DMSO (35.51 ml; 500 mmol) and frozen overnight. Subsequently Py·SO₃ complex (9.5496 g; 60 mmol) was added and reaction was run for ten hours at 60 °C/500 RPM. The mixture was precipitated in 96% ethanol (600 ml) saturated with CH₃COONa·3H₂O (31.5 g) and the separated precipitate solubilized in water and dialyzed. After pre-concentration on vacuum evaporator and adjustment of pH to 9 the solution was cast on Petri dishes and dried at RT to constant weight (QXS, 1.6284 g; N, 1.16; $DS_Q = 0.33$; C, 24.64; H, 4.15; S, 15.91; $DS_S = [\text{sulphur content (\%)/sulphur content of fully substituted anhydroxylose (\%)}] \times 2 = 1.67$; yield = 97%).

The fully sulfated xylan (XS) was prepared by mixing xylan (1.654 g; 10 mmol) with DMF (38.72 ml; 500 mmol) containing Py·SO₃ complex (7.958 g; 50 mmol) and subsequent stirring (500 RPM) at 60 °C for 12 h and worked up as above (2.4483 g; S, 19.00; C, 16.11; H, 3.02; $DS_S = 2.0$; 73% yield).

Partially sulfated xylan SX was obtained under analogous conditions at molar ratio of xylan/DMF/Py·SO₃ complex = 10/500/25 when the experiment was run for only 6 h (SX; 1.624 g; C, 28.34; H, 4.99; S, 6.66; $DS_S = 0.70$; 84% yield). When part of the SX sample (1.2242 g; 5 mmol) was quaternized by dissolving in 15.98 ml of water (1 mol in total) containing 1.6 g NaOH (40 mmol) using 4.48 ml of GTMAC (20 mmol) and treated under analogous conditions as above SXQ (0.7471 g; N, 1.95; $DS_Q = 0.55$; C, 38.49; H, 6.04; S, 3.16; $DS_S = 0.33$) film was prepared.

2.2. Analytical methods

Solution NMR measurements were performed as described previously (Šimković et al., 2011a). The elemental composition of specimens was performed on Macro Analyzer (Elementar Analysensystem GmbH, Donauestr. 7, 63452 Hanau, Germany) at detection ranges for C: 0–150 mg (or 100%); H: 0–15 mg (or 100%); N: 0–100 mg (or 100%) and S: 0–18 mg (or 100%).

SEC-MALS characterization was performed using 0.1 M carbonate buffer at pH 10.0 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).

For AFM analysis the films were dissolved in deionized water with the help of ultrasound (1 h at 60 °C) and obtained a solution which was then filtered through 0.8 μm filter. The films were prepared by casting the obtained solution on glass and drying at 60 °C. Morphological investigations were performed using Nanoscope IIIa AFM microscope (Digital Instruments/Veeco, Santa Barbara, CA), operated in tapping mode. Rectangular silicon cantilevers of model RTESP (Veeco Instruments) were used throughout the study. All scans were performed in air, at room temperature. Height and phase contrast images were recorded simultaneously with a scan frequency below 2 Hz.

For mechanical testing, dog-bone specimens (type B, ISO 527–2) with 10 mm length of the working part were cut. Tensile tests were carried out at 22 °C using an Instron 5800 apparatus at a crosshead speed of 1 mm/min. At least eight specimens were tested for each sample. The stress-at-break (σ_b), elongation-at-break (ϵ_b) and Young's modulus (E) were evaluated.

Wide-angle X-ray diffraction (WAXS) patterns were obtained with a powder diffractometer HZG/4A (Freiberger Präzisionsmechanik GmbH, Germany) and monochromatic CuK α radiation.

Solid state NMR experiments were performed on multinuclear 400 MHz Varian spectrometer operating at 100.54 MHz frequency

for ¹³C NMR experiments and equipped with 4 mm T3-HXY probe working at 10 kHz spinning rate; spin-lattice relaxation time $T_1 = 240$ s for 1024 scans. The sample of measured xylan was in lyophilized form (~50 mg).

TG/DTG/DTA measurements were run on NETSCH STA 449F3 STAF3A-0382 instrument using air environment (50 ml/min) and nitrogen for balance maintenance (PG = 20 ml/min). The sample amounts used were ~30 mg cuts from the films prepared. The heating rate was 10 K/min in Al₂O₃ crucibles.

3. Results and discussion

3.1. Order of chemical modification

According to elemental analysis by quaternization of X at X:NaOH:GTMAC:H₂O = 10/20/20/1000 molar ratio, the trimethylammonium-2-hydroxypropyl- (TMAHP) group was introduced ($DS_Q = 0.55$), and in this way positively charged film QX was prepared in the first step. When sulfated in the second step in DMSO (QX:DMSO:Py·SO₃ = 5/500/60) the fully substituted QXS derivative with $DS_Q = 0.33$ and $DS_S = 1.67$ was obtained. When X was sulfated in DMF with Py·SO₃ complex at 10/500/50 molar ratio, fully substituted xylan sulfate (XS) was prepared. When the ratio was changed to 10/500/25 the DS_S of the product (SX) was only 0.70. By subsequent quaternization of SX at SX:NaOH:GTMAC:H₂O = 5/40/20/100, SXQ film with $DS_Q = 0.55$ and $DS_S = 0.33$ was prepared. The decrease of DS_S indicates that some desulfation took place due to NaOH presence. The NMR data of QX, SX, QXS, and SXQ are listed in Table 1.

According to integration of anomeric protons of QX, $DS_Q = 0.32$ and 16% of xylose units are substituted with 4-O-methyl-D-glucuronate (MeGlcA) units. The chemical shifts of TMAHP-group [55.04/3.22 ppm –N(CH₃)₃; 69.20/3.48 ppm –CH₂N; 65.97/4.39 ppm –CHOH; 74.85/3.71, 3.83 ppm –O–CH₂] as well as all the data listed were obtained by 2D experiments (see Section 2). According to heteronuclear multiple bond correlation (HMBC) experiment the signal of –O–CH₂– (3.71 ppm) of the TMAHP-group is in correlation with C-2 of quaternized xylose unit at 82.34 ppm (Table 1). This indicates that the xylose unit is substituted with quaternary group at C-2 position. Also the difference in chemical shifts of H-2/C-2 atoms of that unit in relation to the values of unsubstituted internal xylose unit confirms the hypothesis.

The partially sulfated sample (SX; Table 1) has almost identical chemical shifts of unsubstituted units observed on QX and also the substituents at H-2/C-2 and H-3/C-3 have dramatically different chemical shift than analogous values for non-substituted xylose units. It also contained 4-O-methyl-D-glucuronic acid units attached to C-2 of 11% of xylose units. Beside those two types of substituents also additional hexose anomeric signal 5.04/92.44 ppm was observed in correlation with signals at 3.90/75.70, 4.26/69.34, 4.00/67.36 ppm and CH₂ group with signals at 3.98, 3.84/61.92 ppm. According to literature it might be related to sulfated cellulose at C-6 (Wang, Li, Zheng, Normakhamatov, & Guo, 2007). This result indicates the presence of cellulose impurities in the used X sample.

The fully substituted QXS was predominantly sulfated at C-3 and the rest of the free C-2 positions of D-xylose units. It did not contain 4-O-methyl-D-glucuronic acid units. Additionally probably all hydroxyls of the TMAHP-groups were sulfated which dramatically affected the NMR data by changing the chemical shifts of hydroxyls of the TMAHP-substituent and both types of quaternized groups are observed. For non-sulfated substituents the shifts were at 3.22/55.08 ppm for N(CH₃)₃; 3.49/69.21 ppm for –CH₂N group; and 4.38/65.93 ppm for –CH(OH)– group, while the –O–CH₂– group could not be assigned. On sulfated

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