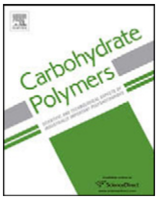
Carbohydrate Polymers 83 (2011) 769–775

Contents lists available at ScienceDirect

Carbohydrate Polymers

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



# Positively and negatively charged xylan films

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ARTICLE INFO

*Article history:*
Received 28 June 2010
Received in revised form 17 August 2010
Accepted 22 August 2010
Available online 27 August 2010

*Keywords:*
Xylan
Film properties
NMR
SEM

ABSTRACT

Xylan was 2-hydroxypropylsulfonated and/or 2-hydroxypropylquaternized for film application. All the products were water soluble with molar masses of the derivatives between $M_n$ of 3.8 and 948.9 kg/mol with polydispersity index $D$ from 1.7 to 26.8. At the range from 100 to 250 μm of thickness the material developed reproducible mechanical properties. When mixed solutions of quaternized and sulfonated samples were used for film preparation, they disrupted although their thickness was 234 ± 18 μm as determined by SEM. The thermal and thermo-oxidative stability of the mixed derivative increased in comparison to unmodified xylan film as determined by TG and DTA analysis. The measured tensile strength values were the best on quaternized films (64.3 MPa) while the Young's modulus values were higher on hydroxypropylsulfonated xylan film (3350 MPa). The mixed derivative gave values close to average between the two derivatives and according to SEM observation also the smoothest surface on the fracture.

## 1. Introduction

Non-cellulosic polysaccharides are important sources for composite preparation (Šimkovic, 2008). (4-O-methyl-D-glucurono)-D-xylan from beech wood is a good candidate due to its linear structure with β-glycosidically linked xylose units and α-glycosidically linked 4-O-methyl-D-glucuronic acid units to C-2 of xylose (Ebringerová, Hromádková, & Heinze, 2005; Šimkovic, Alföldi, & Matulová, 1986). Composites for non-food applications might be produced by covering fiber, paper, wood, and other materials by polysaccharide films. Films from corn stalk xylan, trimethylammonium-2-hydroxypropyl (TMAHP)-xylan and pastes of xylan-sulfate have been already prepared (Goksu, Karamaglioglu, Bakir, Ylmazar, & Yilmazer, 2007; Hettrich et al., 2006; Schwikal, Heinze, Ebringerová, & Petzold, 2006). Also furan-2-carboxylic acid esters of starch, xylan, cellulose, dextran, and curdlan were prepared and the formed films studied with SEM and AFM (Hesse, Liebert, & Heize, 2006). The mechanical properties of arabinoxylan films using plasticizers gave promising results (Mikkanen,Yadav, et al., 2009; Zhang & Whistler, 2004). Also aspen glucuronoxylan was applied for film preparation with xylitol and glucitol as additives (Göndahl, Eriksson, & Gatenholm, 2004). The negative aspects of using alditols as plasticizers, is that by adding them the mechanical properties of formed films diminished.

In the present paper we discuss the films properties of 2-hydroxypropylsulfonate (HPS)-, TMAHP-, their mixture, and HPS/TMAHP-xylan, with a goal to find out how the properties like molar mass, film thickness, and water-solubility, could be affected by the introduction of substituent. The samples were characterized by elemental analysis, 2D NMR spectroscopy, light scattering (SEC-MALLS), TG/DTA, scanning electron microscopy (SEM) and mechanical tester.

## 2. Experimental

### 2.1. Materials

Xylan (X) was extracted from Beech holocellulose with 5% NaOH analogically as for hornbeam wood (Ebringerová, Kramár, & Domanský, 1969). It was not soluble in water and contained 19.3% of carboxyls, 2.93% of methoxyls, and the neutral portion formed on hydrolysis contained 98% of xylose. The water soluble part ($M_w$ 9.275 kg/mol; $D$ 3.8; 0.1 M acetate buffer at pH 4.5 as SEC mobile phase; 35% of recovered mass) represented 15% of X as determined by membrane filtration (Šimkovic, Synytsya, Uhliariková, & Čopíková, 2009). For preparation of unsubstituted water soluble fraction the experiment at X/NaOH/water = 10/40/2000 molar ratio (72 h/60 °C) was run. The pH was attenuated to 7 with HCl and after dialysis and lyophylization 0.0921 g (6% yield) of water soluble part (WSX) and 1.2721 g (77% yield) of water insoluble residue (WIX) was obtained by membrane filtration (100 kDa MWCO, Amicon; under nitrogen pressure of 3.5 kg/cm$^2$).

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doi:10.1016/j.carbpol.2010.08.047

3-Chloro-2-hydroxypropylsulfonic acid, sodium salt (CHPS, Aldrich), (S)-(−)-(3-chloro-2-hydroxypropyl)-trimethylammonium chloride (SCHMAC, 99%; Aldrich), 3-chloro-2-hydroxypropyl-trimethylammonium chloride (CHPMAC, 60%, Serva), and all other chemicals used were of commercial grade and were not further purified.

### 2.2. Hydroxypropylsulfonation

At the ratio of X/NaOH/CHPS/water = 10/20/20/2777 (mmol) the mixture was stirred (500 rpm) for 11 days at room temperature (RT; pH = 8.85). The mixture was concentrated to half of the original volume, precipitated to ethanol, washed with ethanol and the precipitate dissolved in water, concentrated with vacuum evaporator and lyophilized (1.6000 g of 2-hydroxypropylsulfonated xylan [SX; S, 0.74; N, 0; C, 36.94; H, 6.29)]. The degree of substitution {DS = [sample sulfur content (%)/sulfur content of fully substituted anhydroxylose (%)] × 2 = 0.10}. The 4-O-methyl-D-glucoronate content was neglected. From the DS than the yield was calculated from the amount of sample obtained in relation to theoretical yield at determined DS. For SX it was 56%.

When the experiment was run at a ratio of X/NaOH/CHPS/water = 1/20/20/2777, stirred for 7 days at RT, the reaction was stopped by dilution with water. The pH attenuated to 7 and after dialysis (1 kDa MWCO); membrane filtration (100 kDa, Amicon; 3.5 kPa, nitrogen) the part smaller than 100 kDa was lyophilized [0.0586 g of 2-hydroxypropylsulfonated xylan (SX′); S, 1.48; N, 0; C, 31.76; H, 5.66; DS, 0.26; 29% yield].

At the ratio X/NaOH/CHPS/water = 10/40/20/2000 the mixture was stirred for 3 h at 60 °C, pH attenuation with HCl to 8.9, dialysis, filtration (G4 fritted glass, Koch-Light), and vacuum evaporated to 30 mL and after repeated filtration dried on Petri dish at RT to constant weight [1.3819 g of 2-hydroxypropylsulfonated xylan (SX″); S, 1.23; N, 0; C, 34.97; H, 5.89; DS, 0.18; 72% yield] was prepared.

Using the ratio X/NaOH/CHPS/water = 1/40/40/2000 (mmol; 500 rpm) at 60 °C for 6 h, dialyzed, concentrated to about 25 mL, transferred to Petri dish and dried at RT to constant weight (0.1217 g of SXF; S, 0.52; C, 36.41; H, 6.07; DS, 0.07; 68% yield) a film was obtained.

### 2.3. Quaternization

At the ratio of X/NaOH/SCHMAC/water = 1/4/3/200 the reaction was run for 24 h/60 °C and stopped by dilution with water and neutralization to pH 7 with concentrated HCl. After dialysis, filtration, and lyophilization 0.2121 g of 2-hydroxypropyltrimetylammonium xylan {AX; N, 2.71; C, 41.64; H, 7.02; DS = [nitrogen content (%)/nitrogen content of fully substituted anhydroxylose (%)] × 2 = 0.84; 68% yield} was obtained.

When CHPMAC was used at X/NaOH/CHPMAC/water = 10/40/40/2279 for 7 h/60 °C and 17 h/RT, neutralized with HCl to pH 7, dialyzed, preconcentrated and dried on Petri dish at RT to constant weight, 2.0247 g of xylan derivate (AX′; N, 0.61; C, 38.54; H, 7.13; DS, 0.19; 99% yield) was obtained.

### 2.4. Hydroxypropylsulfonation/quaternization

At the ratio X/NaOH/CHPMAC/CHPS/water = 10/120/80/20/557 the reaction was run for 4 h/60 °C, neutralized, dialyzed and dried in Petri dish, 2.1332 g of xylan derivate SAX (S, 1.17; N, 1.62; DS of hydroxypropylsulfonation, 0.54; C, 41.24; H, 7.27; DS of quaternization, 0.17; 46% yield). For SAX the DS for fully substituted product of each substituent was considered to be 1.

### 2.5. Film preparation

Samples (0.1–2 g) were dissolved in 5–30 mL of deionized water, filtered and introduced on the surface of plastic Petri dish (8.5 cm in diameter) to dry out at RT. They were separated from the plastic surface during the drying process without further assistance. When less material than 0.1 g was introduced the films remained bonded on the plastic surface. When more material was used the films were thicker and mechanically more stable. In some cases as listed above the produced derivative was directly dried on Petri dish instead of lyophylization. Films were prepared also by repeating dissolving of the broken pieces of films after mechanical testing without observable effect on the results.

By mixing of sample AX′ (2.5527 g) and SX″ (1.4025 g) with water and dissolution of the components and subsequent drying at RT on Petri dish a film was obtained which disrupted after drying to small pieces not suitable for mechanical testing. This sample (ASX′) was analyzed only by SEM and TG/DTA.

### 2.6. Analytical methods

The elemental analyses of all the samples were performed in duplicate using a Fisons EA-1108 instrument.

NMR measurements were performed in $D_2O$ at 25 °C on Varian 600 MHz UNITY INOVA spectrometer equipped with 5 mm 1H {13C, 15N} PFG Triple Res IDTG600-5 probe head. $^{1}$H and $^{13}$C chemical shifts were referenced to 3-(trimethylsilyl)-propionic acid (TSP) internal standard. Multiplicity edited $^{1}$H-$^{13}$C HSQC spectra were recorded in phase-sensitive pure absorption mode with optimization on one bond coupling constant $^{1}J_{CH} = 165$ Hz. $^{1}$H-$^{1}$H COSY spectra with gradient selection and $^{1}$H-$^{13}$C HMBC spectra were measured in absolute intensity mode. The spectral widths employed in 2D NMR experiments were typically 6000 Hz ($^{1}$H) and 20,000 Hz ($^{13}$C), respectively.

SEC-MALLS characterization was performed using 0.1 M acetate buffer at pH 4.5 or 0.1 M carbonate buffer at pH 10.0 as SEC mobile phase (two TSK PW columns; G4000 and G3000; 35 °C; 0.8 mL/min; $dn/dc = 0.146$ g/ml). The rest of instrument setting was published previously (Šimkovic, Mendichi, & Uhliariková, 2008).

SEM analysis was performed on a Hitachi S - 4700 FEG SEM. The samples were coated with Au/Pd of thickness of about 10 nm in a sputter coater Bal-Tec SCD 500. The cross sections of films were obtained by performing brittle fractures in liquid nitrogen.

Thermogravimetric measurements were run on SDT 2960 (TGA-DTA module; TA Instruments) thermobalance at 90 cm$^3$/min nitrogen or air flow and 10 K/min heating rate from 20 to 1000 °C using 3–24 mg sample amounts in platinum pan.

The mechanical properties of films conditioned at 50 ± 2% humidity and 23 ± 1 °C (24 h) were determined on a universal tensile strength tester INSTRON 1122, Instron Ltd., High Wycombe, Buckinghamshire, England. The jaws distance used was 25 mm at film width of 10 mm. At least five replicated measurements were run for each sample. The thickness of films measured when using micrometer was within 10 μm accuracy.

## 3. Results and discussion

### 3.1. Hydroxypropylsulfonation of (4-O-methyl-D-glucurono)-D-xylan

Because X was only partially soluble in water an experiment was run using the molar ratio of X/NaOH/water at 10/40/2000 to gain water soluble sample (WSX) in 6% yield for NMR analysis. By integration of anomeric signals of the $^{1}$H-NMR spectrum it was calculated that after the treatment only 4% of xylose units were

**Table 1**
NMR data of samples (ppm).

| Sample/unit | $C_1/H_1$ | $C_2/H_2$ | $C_3/H_3$ | $C_4/H_4$ | $C_5/H_5$ | $C_6/H_6$ | $OCH_3$ |
|---|---|---|---|---|---|---|---|
| WSX/MeGlcA | 98.38/5.28 | 71.88/3.56 | 73.07/3.75 | 83.37/3.22 | 72.99/4.32 | 177.60/– | 60.69/3.46 |
| WSX/Xyl[a] | 102.27/4.62 | 76.99/3.43 | 73.23/3.62 | 77.16/3.79 | 63.75/3.42[b] | – | – |
| WSX/Xyl[c] | 102.56/4.48 | 73.60/3.29 | 74.57/3.56 | 77.16/3.78 | 63.78/3.37[d] | – | – |
| SX″/MeGlcA | 98.72/5.28 | 72.31/3.57 | 73.33/3.75 | 83.40/3.22 | 72.92/4.36 | 179.09/– | 61.03/3.46[e] |
| SX″/Xyl[a] | 102.45/4.62 | 77.50/3.44 | 74.00/3.61 | 76.50/3.78 | 63.94/3.43[f] | – | – |
| SX″/Xyl[c] | 102.81/4.30 | 73.87/3.30 | 74.71/3.55 | 77.48/3.77 | 63.93/3.37[g] | – | – |
| AX/MeGlcA | 99.10/5.32 | 72.81/3.60 | 73.38/3.79 | 83.09/3.24 | 73.20/4.36 | – | 61.20/3.48[e] |
| AX/Xyl[a] | 102.66/4.66 | 77.65/3.47 | 74.33/3.66 | 77.58/3.85 | 64.12/4.18[h] | – | – |
| AX/Xyl[c] | 103.21/4.52 | 73.79/3.32 | 75.19/3.59 | 77.88/3.83 | 64.50/4.14[i] | – | – |

[a] Xyl units substituted with MeGlcA unit.
[b] $H_{ax}$ of $CH_2$ of Xyl with $H_{eq}$ at 4.08 ppm.
[c] Xyl units not substituted with MeGlcA.
[d] $H_{ax}$ of $CH_2$ of Xyl with $H_{eq}$ at 4.10 ppm.
[e] Methoxyls.
[f] $H_{ax}$ of $CH_2$ of Xyl with $H_{eq}$ at 4.14 ppm.
[g] $H_{ax}$ of $CH_2$ of Xyl with $H_{eq}$ at 4.09 ppm.
[h] $H_{ax}$ of $CH_2$ of Xyl with $H_{eq}$ at 3.45 ppm.
[i] $H_{ax}$ of $CH_2$ of Xyl with $H_{eq}$ at 3.42 ppm.

substituted with 4-O-methyl-D-glucuronic acid (MeGlcA) units. This is in good agreement with the carboxyl content, according to which the MeGlcA content is 4.45%. This corresponds to DS 0.09 of MeGlcA. According to methoxyls content the MeGlcA content is 0.48%. While X is at the majority water insoluble, by hydroxypropylsulfonation at RT a water soluble polysaccharide was prepared (SX) in 56% yield at X/NaOH/CHPS/water = 10/20/20/2777 molar ratio and DS 0.13. By changing the ratio to 1/20/20/2777 the yield decreased to 29% and DS increased to 0.26 (SX′). When running at 60 °C for 3 h at 10/40/20/2000, the DS slightly increased to 0.18 in comparison to SX with yield of 72% (SX″). At molar ratio of X/40/40/2000 (6 h/60 °C) the yield increased to 68% at DS = 0.07 (SXF). The obtained sample was completely water-soluble.

According to sulfur content the DS of 0.18 was calculated for sample SX″. It means in average every eleventh xylose unit is substituted. According to NMR spectroscopy (COSY, TOCSY, HSQC, and HMBC experiments) the corresponding signals of samples WSX and SX″ were assigned as listed in Table 1. The signals of the 2-hydroxypropylsulfonate groups were at 66.30/4.18 (C/H signal of CHOH) and 53.33/3.23, 3.15 or 3.06 (C/H signals of $CH_2$ groups) ppm. According to the difference in chemical shifts of WSX in comparison to SX″, it seems that the substituent is at both the C-2 as well as C-3 of xylose unit of SX″. The substitution of MeGlcA units was not observed.

### 3.2. Quaternization

After quaternization of X with chiral quaternizing agent (SCHMAC, 99%) at X/NaOH/SCHMAC/water = 1/4/3/200 ratio a high yield (68%) of trimethyl-2-hydroxypropylammonium derivative (AX) at DS of 0.87 was prepared. According to NMR the content of MeGlcA units could not be quantified due to its low concentration and the signals were assigned as listed in Table 1.

When the 60% quaternary agent (CHPMAC) was used at X/NaOH/CHPMAC/water = 10/40/40/2279 ratio at 60 °C for 7 h and after dialysis cast on Petri dish a good quality film was prepared at 99% yield (2.0247 g of AX′; N, 0.61; C, 38.54; H, 7.13) at DS 0.19.

### 3.3. Hydroxypropylsulfonation/quaternization

Mixed derivative ASX′ was prepared using the ratio X/NaOH/CHPMAC/CHPS/water = 10/120/80/20/557 with a slightly smaller content of 2-hydroxypropyl sulfonate than that of 2-hydroxypropyltrimethylammonium group. After dialysis and preconcentration it was casted on two Petri dishes to prepare brown films which remained unbroken. As not equal amounts of the solution were casted on the dishes, the films with different thickness were obtained.

### 3.4. SEC-MALLS analysis

The sample SX″ had the biggest polydispersity from all analyzed samples (Table 2). From the results we assume that the quaternization was less degradative treatment than hydroxypropylsulfonation. In the absence of alkylating agents the sample WSX was degraded the most. All the determined molar masses in carbonate buffer for derivatives SX″, AX, AX′, and SAX were bigger than $M_w$ of WSX as determined in acetate buffer. It indicates that by the modification the insoluble part of the starting material could be solubilized to get a product with bigger molar mass than X. According to the values of recovered mass (Table 2), more of the material was recovered by using of the mobile phase at pH 10. It seams that the ionic groups of prepared derivatives interact with the stationary phase of the SEC column, which results in retaining of some parts of the sample. By quternization/sulfonation in one step, the sample SAX with the biggest molar mass could be prepared.

### 3.5. SEM analysis

As seen on images of WSX and WIX, they both look similar and inhomogeneous on the inner surfaces coming from a film rupture or at the surface of film fracture (Fig. 1a and b). These samples disrupted to small pieces not suitable for mechanical testing with thicknesses of 14.4 ± 0.8 μm for sample WSX and 10.7 ± 0.6 μm for sample WIX, as determined by SEM. At 1 g amount a 100 μm thick film was prepared from WSX as seen on Fig. 1c. As could be seen the films from samples X, WSX, and WIX looked similar. The hydroxypropylsulfonated samples SX and SX″ (Fig. 2a and b) were slightly smoother at the surface of the fracture than that X, although the difference was not dramatic. Surface of AX′ (Fig. 3a) looked sim-

**Table 2**
SEC-MALLS characterization of samples.

| Sample | $M_p$ (kg/mol) | $M_w$ (kg/mol) | $D = M_w/M_n$ | Recovered mass (%) |
|---|---|---|---|---|
| WSX | 4.2 | 7.6 | 2.0 | 64.2 |
| SX″ | 21.7 | 402.0 | 26.8 | 50.5 |
| AX | 27.7 | 20.5 | 1.7 | 42.0 |
| AX′ | 20.0 | 24.0 | 2.4 | 9.9 |
| SAX | 1194.6 | 948.9 | 11.6 | 36.3 |

$M_p$, molar mass at a peak; $M_w/M_n$, polydispersity index; $M_w$, weight-average molar mass; $M_n$, numeric-average molar mass.

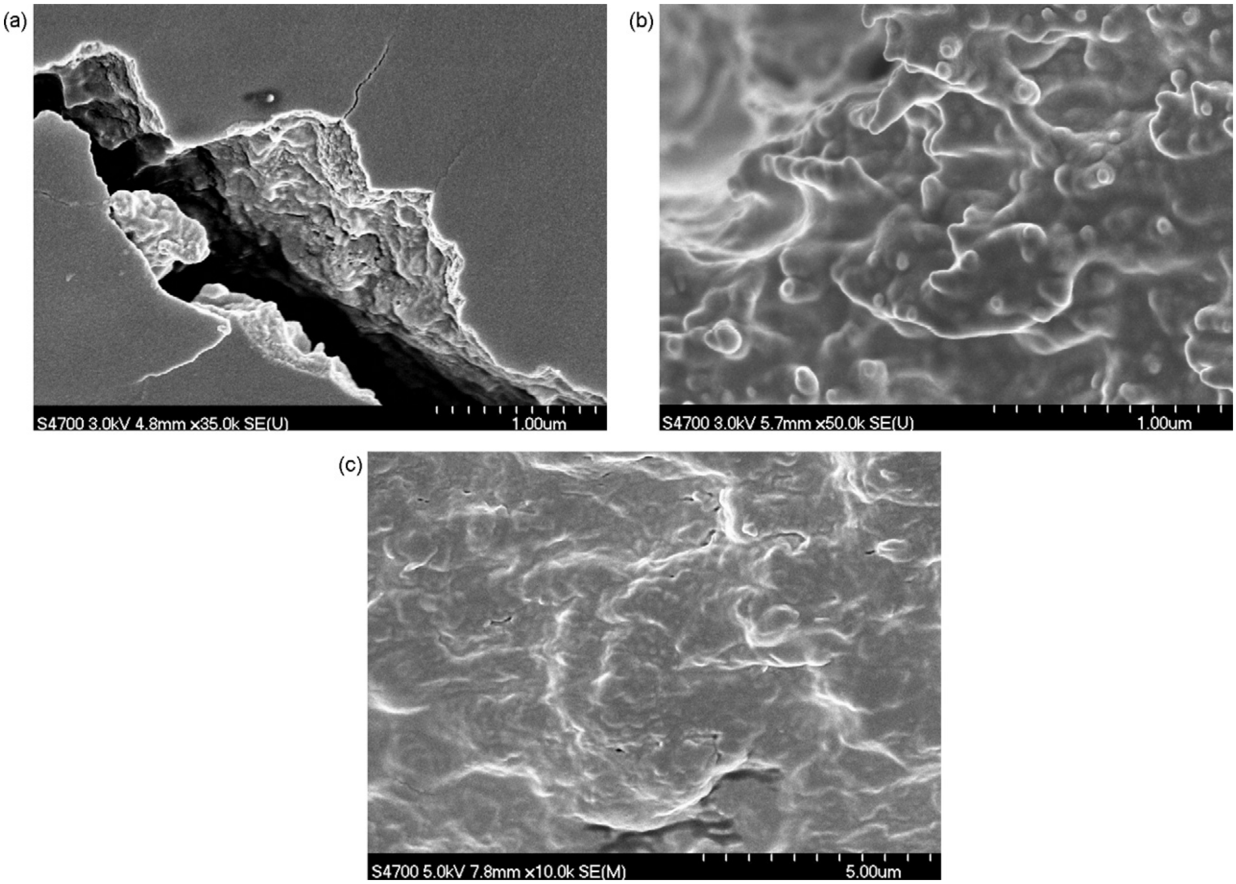

**Fig. 1.** SEM images of the surface of WSX film on a surface/fracture (a), WIX (b), and WSX film (c) on the surface of the fracture.

ilarly like X in Fig. 1a. The image of the fracture of AX′ was similar, but slightly smoother than X, SX or SX″ (Fig. 3b). The film of SAX on the fracture (Fig. 4a) looked smoother than SAX′ (Fig. 4b) prepared from samples SX″ and AX′ by casting from mixed solutions as well as all the other samples analyzed by SEM. The images were comparable with surfaces of samples obtained on films from other xylan sources (Goksu et al., 2007; Zhang & Whistler, 2004).

### 3.6. Thermal analysis features

Films were analyzed in nitrogen and air using the TG and DTA method (Table 3). All the samples contained about 15% of water which was released by heating up to 200 °C. The starting material X had the first DTA peak at 259 °C and DTG maximum at 287 °C in nitrogen environment. There were four additional DTA maxima at 287, 452, 825, and 979 °C. The residue at 1000 °C was 11%. In air environment the first DTA peak was at 284 °C, while the first DTG maximum was at 269 °C. The second DTA and DTG maxima were at 446 °C. The residue at 1000 °C was just 1%. The samples WSX and WIX prepared by alkaline pretreatment exhibited the first DTA peak in nitrogen at 235 and 267 °C, respectively. The DTG peak was similar for both the water soluble WSX and insoluble sample WIX. There were additional DTA maxima at 323, 352, and 428 °C for WSX and 7% residue in nitrogen environment at 1000 °C. In air the DTG values for WSX indicated the presence of inorganics with 6% residue at 1000 °C. Sample WIX gave 0% residue at 1000 °C in nitrogen as well as in air environment. There were only three DTA maxima for WIX in air environment. By the chemical modification the DTA and DTG maxima of sample SX were moved to higher temperature than for samples X, WSX and WIX. There were four DTA and three DTG maxima for sample SX in inert environment and only two DTA and DTG maxima in air environment. For SX″ with higher DS than SX in inert environment the observed thermal stability was slightly better than for samples SX and X up to 500 °C. In air environment sample SX″ is more stabile up to 500 °C than X and SX. According to DTA the main thermo-oxidation exotherm of SX″ is at 491 °C while for X this step is at 446 °C. The quaternized sample AX degraded in inert environment showing first DTA and DTG peaks at 274 and 277 °C in inert environment (Table 4). This is higher than for SX″. For sample AX′ with lower DS the temperature was at 263 °C for both peaks. The rest of the DTA curve for AX was endothermic while for AX' exotherms were observed at 488 and 754 °C. In air environment two exotherms were observed at 279 and 461 °C for AX and at 264 and 377 °C for AX′. There were no inorganics present in both samples which was proved by 0% residue at 1000 °C. For the mixed derivative SAX there were three exotherms observed at 273, 376 and 565 °C in inert environment and one DTG peak at 268 °C, which is close to values observed on sulfohydroxypropylated samples AX and AX′. In oxidative atmosphere only two exotherms were observed with a shoulder around 400 °C. This indicates some synergistic effect of the two groups in the thermooxidation process. The residue in air environment at 1000 °C was 0%, which indicates there were no inorganics present. The mixture of derivatives SX″ and AX′ (SAX′) was degraded under inert and oxidative conditions at lower temperatures than SAX. Both DTA and DTG peaks were at lower temperature than for SAX, which indicates better thermal properties for the mixed ether than sample prepared by mixing two different derivatives containing the quaternary and sulfonated derivatives on different polysaccharides. The residues in inert and oxidative environment at 1000 °C indicate the presence

**Table 3**
Thermal analysis of unmodified and hydoxypropylsulfonated samples.

| Sample | Atmosphere | DTA peaks | | DTG peaks | | Residue (%) at (°C) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | (°C) | *Δ* (°C/mg) | (°C) | Max. rate (mg/min) | 200 | 300 | 400 | 500 | 1000 |
| X | Nitrogen | 259 | −0.170 | 287 | 0.99 | 85 | 41 | 32 | 27 | 11 |
| | | 287 | −0.172 | | | | | | | |
| | | 452 | −0.168 | | | | | | | |
| | | 825 | −0.149 | | | | | | | |
| | | 979 | −0.121 | | | | | | | |
| | Air | 284 | −0.205 | 269 | 0.61 | 84 | 41 | 30 | 4 | 1 |
| | | 446 | 1.282 | 446 | 0.34 | | | | | |
| WSX | Nitrogen | 235 | −0.256 | 272 | 0.40 | 84 | 49 | 39 | 34 | 7 |
| | | 323 | −0.264 | 800 | 0.14 | | | | | |
| | | 352 | −0.265 | | | | | | | |
| | | 428 | −0.261 | | | | | | | |
| | Air | 275 | −0.024 | 260 | 0.55 | 85 | 48 | 39 | 33 | 6 |
| | | 367 | −0.200 | 459 | 0.06 | | | | | |
| | | 479 | −0.200 | 599 | 0.29 | | | | | |
| | | 599 | 0.555 | 868 | 0.02 | | | | | |
| | | 685 | −0.246 | | | | | | | |
| | | 943 | −0.246 | | | | | | | |
| WIX | Nitrogen | 267 | −0.207 | 274 | 0.87 | 83 | 38 | 29 | 24 | 0 |
| | | 343 | −0.239 | 357 | 0.09 | | | | | |
| | | 412 | −0.227 | 883 | 0.12 | | | | | |
| | | 465 | −0.227 | | | | | | | |
| | Air | 270 | −0.185 | 270 | 0.81 | 83 | 39 | 27 | 0 | 0 |
| | | 343 | −0.078 | 432 | 0.54 | | | | | |
| | | 462 | 2.901 | | | | | | | |
| SX | Nitrogen | 285 | −0.323 | 283 | 0.47 | 81 | 42 | 31 | 22 | 0 |
| | | 449 | −0.308 | 489 | 0.08 | | | | | |
| | | 670 | −0.284 | 787 | 0.09 | | | | | |
| | | 755 | −0.294 | | | | | | | |
| | Air | 289 | −0.300 | 280 | 0.37 | 81 | 41 | 30 | 5 | 0 |
| | | 464 | 0.548 | 466 | 0.26 | | | | | |
| SX″ | Nitrogen | 257 | −0.460 | 257 | 0.44 | 85 | 47 | 35 | 30 | 4 |
| | | 718 | −0.440 | 339 | 0.06 | | | | | |
| | | 944 | −0.407 | 839 | 0.06 | | | | | |
| | | | | 893 | 0.06 | | | | | |
| | Air | 261 | −0.299 | 261 | 0.55 | 86 | 46 | 29 | 10 | 5 |
| | | 347 | −0.154 | 327 | 0.09 | | | | | |
| | | 491 | 0.608 | 491 | 0.24 | | | | | |
| | | 943 | −0.246 | | | | | | | |

**Table 4**
Thermal analysis of quaternized and mixed derivatives.

| Sample | Atmosphere | DTA peaks | | DTG peaks | | Residue (%) at (°C) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | (°C) | *Δ* (°C/mg) | (°C) | Max. rate (mg/min) | 200 | 300 | 400 | 500 | 1000 |
| AX | Nitrogen | 274 | −0.138 | 277 | 0.99 | 83 | 34 | 26 | 20 | 0 |
| | | 353 | −0.211 | 924 | 0.31 | | | | | |
| | | 523 | −0.259 | | | | | | | |
| | | 876 | −0.369 | | | | | | | |
| | Air | 279 | −0.055 | 269 | 0.79 | | | | | |
| | | 461 | 0.612 | 453 | 0.30 | | | | | |
| | | 519 | 0.028 | 509 | 0.08 | | | | | |
| | | 929 | −0.260 | | | | | | | |
| AX′ | Nitrogen | 263 | −0.110 | 263 | 1.31 | 85 | 33 | 26 | 21 | 0 |
| | | 488 | −0.207 | 390 | 0.16 | | | | | |
| | | 754 | −0.220 | | | | | | | |
| | Air | 264 | −0.074 | 263 | 1.32 | 85 | 35 | 25 | 0 | 0 |
| | | 377 | 0.129 | 466 | 0.48 | | | | | |
| | | 480 | 0.727 | | | | | | | |
| SAX | Nitrogen | 273 | 0.086 | 268 | 1.83 | 85 | 42 | 32 | 26 | 12 |
| | | 376 | 0.000 | | | | | | | |
| | | 565 | −0.044 | | | | | | | |
| | Air | 276 | 0.134 | 270 | 1.57 | 85 | 43 | 30 | 13 | 0 |
| | | 521 | 1.085 | 505 | 0.78 | | | | | |
| SAX′ | Nitrogen | 253 | 0.042 | 250 | 1.89 | 88 | 41 | 32 | 27 | 17 |
| | | 307 | −0.044 | | | | | | | |
| | | 479 | −0.031 | | | | | | | |
| | Air | 265 | 0.106 | 255 | 2.00 | 88 | 41 | 28 | 3 | 2 |
| | | 462 | 1.192 | 458 | 0.95 | | | | | |

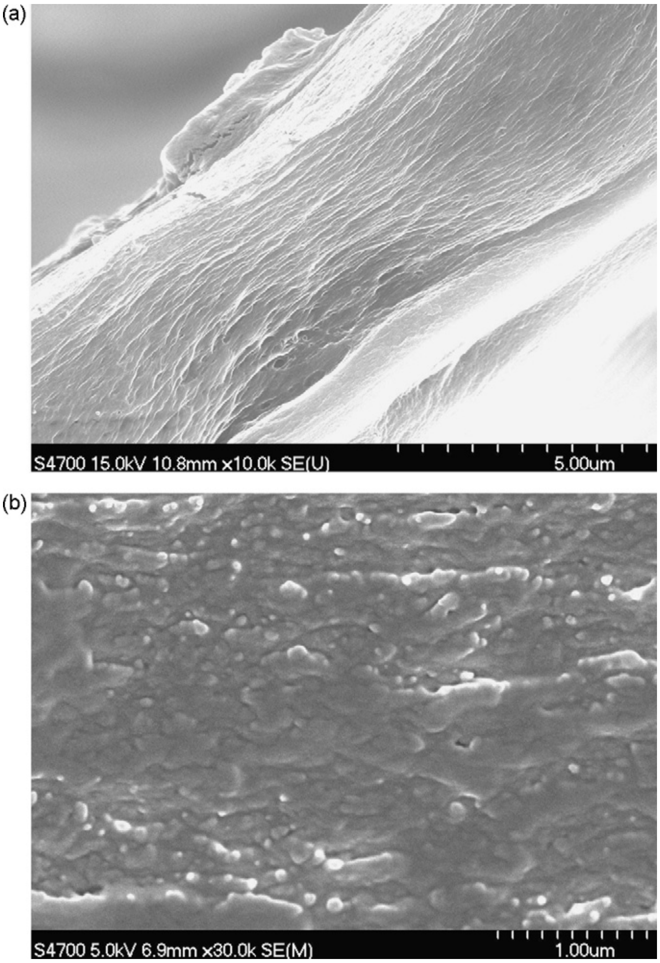

**Fig. 2.** SEM images of films made from samples SX (a) and SX″ (b), both taken from the surfaces of the fractures.

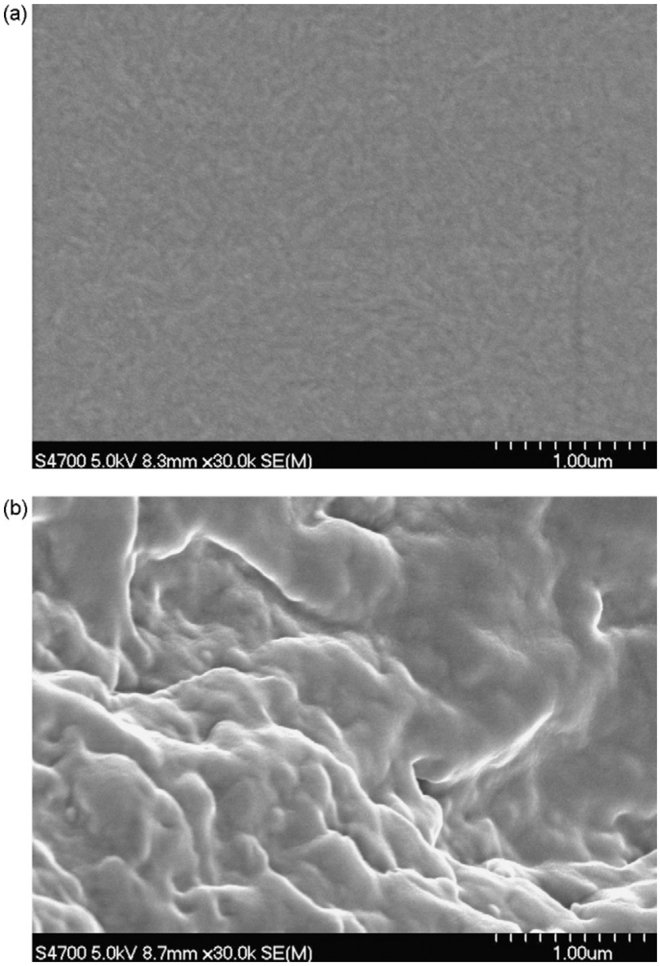

**Fig. 3.** SEM images of the film surface of sample AX′ (a) as well as on the surface of the fracture (b).

of some inorganics originating probably from sample SX″ due to its 5% residue in air at 1000 °C.

### 3.7. Mechanical properties

The film from WSX demonstrated increasing tensile strength and Young's modulus with increasing thickness (Table 5 ). It has smaller tensile strength than arabinoxylan from wheat straw (Zhang & Whistler, 2004), but films from xylan from cotton stalk with lignin content resulted in smaller tensile strength than X (Goksu et al., 2007). The data on oat spelt arabinoxylan gave similar tensile strength at 40% plasticizer content and smaller values of Young's modulus than X (Mikkonen, Heikinnen, et al., 2009). There are no data on molar masses in the citied references, but the molar mass of WSX was the lowest from all studied samples. With increasing degree of hydroxypropylsulfonation the Young's modulus of SX″ increased in comparison to samples SX and X. With increasing thickness Young's modulus, tensile strength, and elongation of SX″ increased. The quaternized sample AX with higher nitrogen content than AX′ also gave smaller value of Young's modulus than samples AX′, SX″, SX, and X. The tensile strength value of sample AX' at 220 μm thickness was the biggest from all analyzed samples. This sample was thicker than all the previous samples. The molar mass ($M_w$) of sulfonated samples was bigger than for quaternized material. It indicates that this phenomenon is not the predominant factor for increased tensile strength (TS) because TS was bigger for quaternized than for sulfonated samples. On the other side the Young's modulus values increased with its increase of $M_w$. The mixed ether derivative SAX at 250 μm thickness gave fear results of both Young's modulus and tensile strength although

**Table 5**
Mechanical properties of studied xylan films.

| Sample | X | X | SX | SX″ | SX″ | AX | AX′ | AX″ | SAX | SAX |
|---|---|---|---|---|---|---|---|---|---|---|
| YM (MPa)[a] | 499 | 2084 | 1990 | 2896 | 3350 | 486 | 1772 | 2471 | 1516 | 1717 |
| TS (MPa)[b] | 5.75 | 21.02 | 26.69 | 16.83 | 20.70 | 12.73 | 36.07 | 64.26 | 17.42 | 47.51 |
| Elongation (%) | 0.77 | 1.03 | 1.88 | 0.60 | 0.97 | 3.28 | 2.32 | 4.23 | 1.26 | 4.28 |
| Thickness (μm) | 40[c] | 100[c] | 210[c] | 104[d] | 160[c] | 60[c] | 150[c] | 220[c] | 81[d] | 250[c] |

[a] Young's modulus.
[b] Tensile strength.
[c] Measured with micrometer.
[d] Measured by SEM.

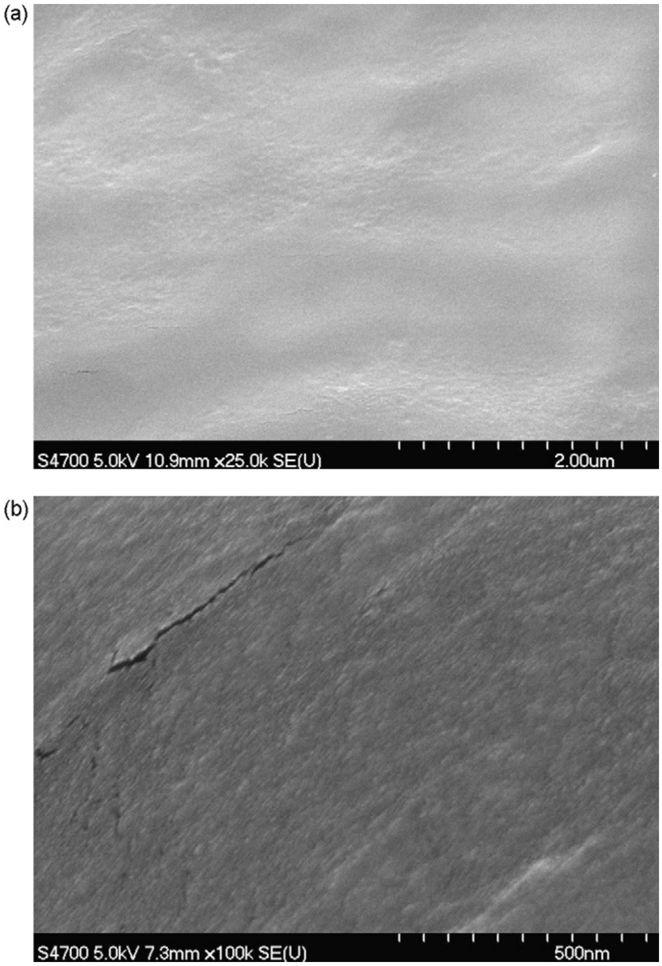

**Fig. 4.** SEM images of the surfaces of films made from mixed derivatives SAX (a) and SAX′ (b).

AX′ at 220 μm thickness gave better results. The biggest Young's modulus was observed on 160 μm thick sample SX″.

## 4. Conclusions

Films from Beech wood xylan, TMAHP-xylan, HPS-xylan, and mixed derivatives were prepared and tested. The mechanical properties were comparable with films prepared on xylan from different sources. The films were water soluble and with an increasing thickness the properties were improved and were reproducible also by repeating film preparation from broken films after mechanical testing. The thermal stability of the mixed derivative was better than for the starting material. According to the SEM observation this derivative also had the smoothest surface on the fracture.

## Acknowledgements

The authors are pleased to acknowledge Maria Matulová, Slovak Grant Agency VEGA (Project No. 2/7030/7), APVV-0650-07, and Slovak State Program Project No. 2003SP200280203 for the support and helpful discussion. This work was also supported by the research program MSM 6046137302 preparation and research of functional materials and material technologies using micro and nanoscopic methods.

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