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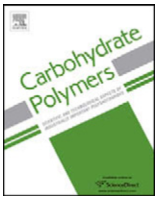

Flexible oxygen barrier films from spruce xylan

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ABSTRACT

Arabinoglucuronoxylan was extracted from Norway spruce and films prepared by casting from aqueous solution. The sugar analysis and NMR confirmed that the spruce xylan was composed of arabinose, 4-O-methyl-glucuronic acid and xylose in a ratio of 1:2:11 respectively. Substitutions of 4-O-methyl-α-D-Glc*p*A at O_2 and of α-L-Ara*f* at O_3 on the xylose backbone were found by NOE analysis. NOE cross-peaks indicated as well that there is at least one free xylose on the main chain present between two substitutions. Whether the distribution of side chains was random or in blocks was uncertain. The average molecular weight of the sample was determined by size exclusion chromatography to be 12,780 g/mol. Arabinoglucoronoxylan casting yielded transparent flexible films with an average stress at break of 55 MPa, strain at break of 2.7% and a Young's Modulus 2735 MPa. Wide-angle X-ray scattering analysis showed that the arabinoglucuronoxylan films were totally amorphous. Addition of sorbitol as plasticizer resulted in less strong but more flexible films (strain at break of 5%). Peaks of crystallinity could be seen in X-ray which corresponds to sorbitol crystallizing in distinct phases. The dynamic mechanical analysis showed that the arabinoglucuronoxylan film softened at a later relative humidity (80% RH) in comparison with plasticized films (60% RH). The films showed low oxygen permeability and thus have a potential application in food packaging.

1. Introduction

Packaging material affects our everyday life and comprises approximately 66% of the post-consumer plastic waste in Europe (APME, 2009). The heightened social and environmental consciousness in conjunction with strict regulations on pollutants and disposal of waste products have increased the industries need to find new solutions to improve recycling streams and reduce the consumption of fossil fuels (Marsh & Bugusu, 2007). The most common barrier materials in today's food packages are either aluminium or various synthetic plastics (Lange & Wyser, 2003). Commercialization of bioplastics, biopolymers from renewable resources, is on its way and may serve as a new environmental source for barrier material that may also reduce the solid waste by being biodegradable (Marsh & Bugusu, 2007).

Today bioplastics represent less than 0.25% of the total plastics market (APME, 2009). The goal of a food packaging is to protect the food from contamination and oxidation and thereby extend its shelf life. For that reason it is essential that the packaging material works as an oxygen barrier and prevents the gain of moisture (Robertson, 2009). The packaging film must also have good mechanical strength and a certain degree of flexibility (Hartman, Albertsson, Lindblad, & Sjöberg, 2006). The use of biopolymers, such as polysaccharides, as film barrier materials has received increased interest due to their vast abundance and great oxygen barrier properties (Bourtoom, 2009; Hartman et al., 2006; Huber & Embuscado, 2009).

The most abundant renewable raw material on Earth is wood. Wood is composed primarily of cellulose, hemicelluloses and lignin (Sjöström, 1993). Norway spruce (*Picea abies*) is a predominant softwood species in the European forest, and is mainly used in the pulp and paper industry (Bertaud & Holmbom, 2004). The wood hemicelluloses are extracted in the pulp and paper process but so far there is no retrieval of the polysaccharides which are today seen as a source for the development of new products (Suurnäkki, Tenkanen, Buchert, & Viikari, 1997). The major hemicelluloses in Norwegian spruce are galactoglucomannans and arabinoglucuronoxylans (Timell, 1967; Willför, Sundberg, Hemming, & Holmbom, 2005).

Past research has shown that hemicelluloses have the ability to form plastic like films and coatings. Arabinoxylan from barley husk has been shown to form flexible films without plasticizer. The amorphous films were strong (stress at break 50 MPa) but highly hygroscopic (Höije, Gröndahl, Tømmeraas, & Gatenholm,

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2005). Glucuronoxylan on the other hand needs a plasticizer in order to form films. Gröndahl et al. studied the addition of xylitol and sorbitol in different ratios. The films were semicrystalline (44–47%) and films were stronger (stress at break 40 MPa) and less flexible with less amount of plasticizer. The 35% (w/w) sorbitol film had an oxygen permeability of 0.21 at 50% RH. This value is identical to the oxygen permeability of poly(vinyl alcohol) (PVOH) film, which is an excellent oxygen barrier material (Gröndahl, Eriksson, & Gatenholm, 2004; Sapalidis, Katsaros, Romanos, Kakizis, & Kanellopoulos, 2007).

The disadvantages with polysaccharides are their hygroscopic nature which results in a low protection level against water (Huber & Embuscado, 2009; Kester, 1986). This can be solved by either laminating the polysaccharide with a water barrier film or chemically modifying the polymer. Gröndahl et al. studied the surface gas-phase fluorination of arabinoxylan films. The aim was to make the barley husk arabinoxylan films hydrophobic. The modification resulted in decrease moisture content from 18 to 12% (Gröndahl, Gustafsson, & Gatenholm, 2006).

Peroval et al. (2004) investigated cold plasma and electron beam (EB) irradiation to improve the water vapor barrier properties of arabinoxylan films by grafting hydrophobic acrylate monomers onto the surface. The treated arabinoxylan films pre-activated with EB followed by impregnation with additional monomer and a second EB irradiation resulted in a 67% decrease in water vapor permeability (WVP).

Hartman et al. (2006) developed films with low OP and good mechanical properties from O-acetyl-galactoglucomannan (AcGGM) films. The films were formed by solution-casting from water with the addition of plasticizers such as glycerol, sorbitol and xylitol. The films showed poor results for oxygen permeability. When a binary system of AcGGM and alginate or carboxymethylcellulose (CMC) was used, the mechanical strength and resistance towards humidity increased. The films containing alginate and CMC had an oxygen permeability of 0.55 and 1.28 respectively at 50% RH.

The aim of the present study was to structurally characterize spruce arabinoglucuronoxylan and to examine its film properties from a food packaging application perspective.

2. Experimental

2.1. Materials and isolation

Arabinoglucuronoxylan (AGX) was extracted from Norway spruce by alkali extraction based upon the Wise and Timell methods (Timell, 1961; Wise, Murphy, & D'Addieco, 1946). In brief, 150 g of wood meal was delignified with sodium chlorite in a three-necked round flask, in the following manner: 1:25 wood to liquor ratio was adjusted with water and set to a temperature of 70–80 °C. The first load of reagents, composed of glacial CH_3COOH and $NaClO_2$ (15 ml: 45 g respectively), was added to this suspension, and then every 12 h the same amount of reagents were loaded to the reaction mixture four more times. About 100 g of hollocelulose were obtained, which was then extracted with 24 wt.% KOH in a ratio 1:7 w:v for 24 h at room temperature. Hemicelluloses were precipitated from the extract with acidic ethanol (hemicellulose solution:EtOH 96%:glacial CH_3COOH in a ratio 1:4:0.4 v:v:v respectively) which were afterwards filtrated and dried. Hemicelluloses were again dissolved in 10 wt.% KOH (1:10 w:v) at room temperature for about 30 min and then the solution was treated with a saturated solution of $Ba(OH)_2$ (1:20 w:v) in order to precipitate the galactoglucomannans which afterwards were separated by centrifugation. The supernatant containing AGX was poured into a solution of acidic ethanol as described above in order to obtain AGX with a yield of approximately 10 g (7 wt.% from the original wood).

2.2. Composition analysis

The sugar content was determined by an ICS-3000 Dionex (Dionex, Sweden). The system was equipped with a gradient pump; column oven; autosampler and one guard column followed by AEC column capable of separating monosaccharide's (ProPac PA 4 × 250 mm, CarboPac PA 4 × 250 mm). AGX was first impregnated with 72% sulfuric acid (200 mg AGX, 3 ml of H_2SO_4) (Theander & Westerlund, 1986) under vacuum for 15 min followed by warming in a water bath (30 °C) for 1 h. Deionized water (84 ml) was added, diluting the sulfuric acid to a final concentration of 2.5%, and the sample was then autoclaved at 125 °C for 1 h. The material was filtered through a PVDF filter (GV, Millipore, 0.22 μm). The filtrate was collected and the volume was adjusted to 100 ml with deionized water. 5 ml of the sample was added to a volumetric flask (50 ml) along with 5 ml fucose (400 mg/l) as an internal standard. The volume was adjusted with deionized water. A part of the sample was filtered again into 1.5 ml vials (GHP, PALL, 0.45 μm). The arabinose to xylose ratio was calculated by relating the area of the recorded peaks to the known fucose concentration. The Klasson lignin was also determined gravimetrically as the insoluble material after hydrolysis according to the Uppsala method (Theander, Aaman, Westerlund, Andersson, & Pettersson, 1995). The 4-O-methylglucuronic acid was determined using enzymatic hydrolysis of arabinoglucuronoxylan followed by capillary zone electrophoresis as described elsewhere (Dahlman, Jacobs, Liljenberg, & Olsson, 2000).

2.3. Nuclear magnetic resonance (NMR) spectroscopy

The ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance III 600 MHz spectrometer using a 5.0 mm $^1H/^{13}C/^{15}N/^{31}P$ inverse detection QXI probe, equipped with z-gradients and controlled by Topspin 2.1 software. The NMR spectra were obtained for ^2D_2O solution of approximately 20 mg polysaccharide at 25 °C. The chemical shifts were referenced using acetone (δ_H 2.225, δ_C 31.05) as internal reference. The data were acquired and processed using Bruker Topspin software. The signals were assigned using 1D and 2D experiments, TOCSY, NOESY, HSQC, HSQC–TOCSY and HMBC from the Bruker library. The relaxation delay between successive pulse cycles was 1.5 s for COSY and TOCSY and 2 s for NOESY. The TOCSY experiments were carried out with mixing times of 30 and 90 ms, NOESY with 100 and 300 ms, HSQC–TOCSY experiment with 80 ms, and HMBC with 60 ms.

2.4. Size exclusion chromatography (SEC)

The molecular weight of the arabinoglucuronoxylan was determined using a HPSEC–MALS–RI–UV aqueous system consisting of a Waters 2690 (Waters Corporation, Milford, MA, USA). The system had an online degasser; auto sampler; column oven and three serial connected columns (Shodex OHpak SB-803, 804 and 806 M HQ) controlled at 50 °C. The detectors were multi-angle laser light scattering (MALS; DSP equipped with a He–Ne laser at 632.8 nm, Wyatt Technology Corp., Santa Barbara, CA, USA); refractive index (RI) controlled at 35 °C (Optilab DSP, Wyatt Technology Corp.) and a UV–vis detector set to record at 280 nm (Shimadzu SPD-10A, Shimadzu Corp., Kyoto, Japan). The eluent used was sodium nitrate (0.1 M $NaNO_3$) containing 0.02% sodium azide (NaN_3). The flow rate was 0.4 ml/min. All samples were dissolved in 0.1 M $NaNO_3$ solution at a concentration of 2% (w/w) and filtered (GHP syringe filter, 0.45 μm, PALL). The d*n*/d*c* used was 0.146 ml/g (Dervilly et al., 2002). The range of angles available for determination was 30–150°. The weight–average molecular weight was determined using ASTRA3 software. The SEC was also run in a strongly alkaline sodium hydroxide/acetate solution (0.2 M hydroxide and 0.1 M acetate, pH 13) according to previously described method (Jacobs, Lundqvist, Stålbrand, Tjerneld, & Dahlman, 2002).

2.5. *Preparation of films*

Films were prepared by mixing xylan alone and xylan plus sorbitol with deionized water under magnetic stirring at 70 °C for 15 min. The total amount of dry substance in each film was kept constant at 2.5% (w/w). Sorbitol was added at 5, 15 and 25 wt.% with respect to the xylan mass. The solutions were poured onto polystyrene petri dishes. The films were dried at 25 °C and a relative humidity (RH) of 30, 50 and 70%. No difference in either crystallinity or mechanical properties were seen as an effect of different humidity when film was formed which is why 50% RH was used thereafter. The formed films were conditioned at 50% RH before characterization.

2.6. *Tensile testing*

The mechanical properties of the conditioned arabinoglucuronoxylan films were determined by a tensile testing machine (Lloyd L2000R) with a load cell of 100 N. The method used was pull to break. The test took place at room temperature (25 °C) at a fixed humidity (50% RH). The samples were cut into strips 9.4 mm in width using a punch. The thickness of the samples was determined by a micrometer (Mitutoyo, Japan). The gauge length was set to 35 mm, speed at 5 mm/min and preload at 0.5 N. For each sample, at least five replicas were made. The stress and strain at break were recorded and the Young's modulus calculated using Nexygen MT software (Ametek, FL, USA).

2.7. *Dynamic mechanical analysis (DMA)*

DMA was used to measure the storage modulus (G') and loss modulus (G''). Humidity scan was used to analyze the softening of the arabinoglucuronoxylan films. The scan was performed in a DMA Q800 (TA Instruments, New Castle, DE, USA), which had an extensiometer connected to a humidity controller. The films were cut into strips (9.4 mm × 10 mm). The samples were loaded at 1 Hz frequency, 125% force track and amplitude at 5 μm. The temperature was fixed at 25 °C and the humidity ramp was 1% RH per 10 min starting at 0% up to 90% RH.

2.8. *Wide angle X-ray scattering (WAXS)*

The crystallinity of the xylan films was determined using a Siemens D5000 goniometric diffractometer (Munich, Germany). The film was placed in goniometer using a sample holder (ø3 cm). Diffractograms were recorded in the reflection geometry using Cu Kα radiation with a wavelength of 1.54 Å. The 2θ was varied between 5° and 50° at a rate of 1° (2θ) per minute, a step size of 0.1 (2θ) and the divergence split fixed to 0.5 mm.

2.9. *Oxygen permeability*

The oxygen diffusion of the films was measured by Systech 8001 permeation analyzer (Systech Instruments, UK) in accordance with ASTM D3985-81. The test conditions consisted of: nitrogen stream, which is routed through the inner half of the test cell, and oxygen, which is supplied into the outer half. Oxygen permeates the test material and is picked up by nitrogen gas flowing through the inner half. The amount of oxygen carried by the carrier gas is measured using a coulometric oxygen sensor, to determine the oxygen transmission rate. The temperature and relative humidity of the test conditions were 25 °C and 50% RH, respectively. The final transmission rate was recorded when a stable duplicate samples were measured. The area of samples was 5 cm^2 and the analysis was made in 50% RH after conditioning of the samples.

3. Results and discussion

3.1. *Material and isolation and chemical composition*

Sodium chlorite is a mild delignification reagent quite useful for research purposes since alpha cellulose and hemicelluloses (holocellulose) can be obtained with minimum manipulation, and low carbohydrate loses. The Wise method (acidic sodium chlorite), is especially effective with softwoods and delignification of spruce by this method allows quantitative removal of hemicelluloses (Wise et al., 1946). Extraction of hemicelluloses from holocellulose was achieved with KOH and separation of galactoglucomannans was carried out through complexation with Ba(OH)$_2$. In our modified method for isolation of arabinoxylan, the delignification time was extended to 60 h making a more intensive delignification both in time and load of reagents. This may result in lower holocellulose yields, since cell wall polysaccharides can be lost due to hydrolytic and oxidative reactions. Despite that fact, we obtained 7.0 wt.% (84% yield) AGX from wood (7.6% pentosan content in the spruce wood by Tappi, UM 236, which corresponds to 8.3 wt.% AGX) and highly purified as seen in the chemical composition (*vide infra*).

The chemical composition of the isolated arabinoglucuronoxylan was determined using Dionex either by enzymatic or acid hydrolysis and contained (w/w) 80.5% xylose, 10.0% 4-O-methylglucuronic acid, 6.9% arabinose and 2.3% other sugars (mannose, glucose and galactose). It is noteworthy to point out the high amount of glucuronic acid in spruce AGX, which might have a great effect on the materials properties of products derived from these hemicelluloses. The Timell method was originally designed for isolation of galactomannans and galactoglucomannans, and separation of hemicelluloses based upon this method yielded the recovery of a highly purified AGX as shown in the carbohydrate analysis.

3.2. *NMR characterization*

The structure of the spruce xylan was analyzed by ^{1}H and ^{13}C NMR. The assignment of the proton signals was obtained from ^{1}H–^{1}H TOCSY and ^{1}H–^{13}C HSQC–TOCSY NMR spectra while the carbon signals were assigned from ^{1}H–^{13}C HSQC (Fig. 1) and HSQC–TOCSY. The inter-residue linkages were identified from NOESY and HMBC spectra. The ^{1}H NMR spectrum is shown in Fig. 2. The anomeric signals are found in two spectral regions: δ5.5–5.2 and 4.7–4.4. The signal at 5.38 ppm is from the anomeric proton signal of a α-L-Ara*f* (A) residue (1→3)-linked to a β-D-Xyl*p* group (Xyl-D) (Table 1, Fig. 2). The signal at 5.27 ppm was assigned to the anomeric proton of a 4-O-methyl-α-D-Glc*p*A acid residue (B) (1→2)-linked to a β-D-Xyl*p* group (Xyl-C). The ^{1}H and ^{13}C NMR chemical shifts of these side chains sugars and of the xylose sugars to which they are linked are in good agreement with previously published data on similar compounds (Verbruggen et al., 1998; Hoffmann, Leeflang, de Barse, Kamerling, & Vliegenthart, 1991). The existence of a (1→2)-linkage between 4-O-methyl-α-D-Glc*p*A (B) and β-D-Xyl (C) was confirmed by the observation of a NOE cross peak between H-1 of B and H-2 of C. The (1→3)-linkage between α-L-Ara*f* (A) and β-D-Xyl (D) was confirmed by the observation of a NOE cross peak between H-1 of A and H-3 of D (Table 2).

At least five different chemical environments were observed for the Xyl residues (C–G). The large signal at 4.47 ppm was assigned to the anomeric proton of the unsubstituted Xyl residues of the main chain (E). It was not possible to determine whether the distribution of the α-L-Araf-(1→3) and 4-O-methyl-α-D-Glc*p*A-(1→2) side

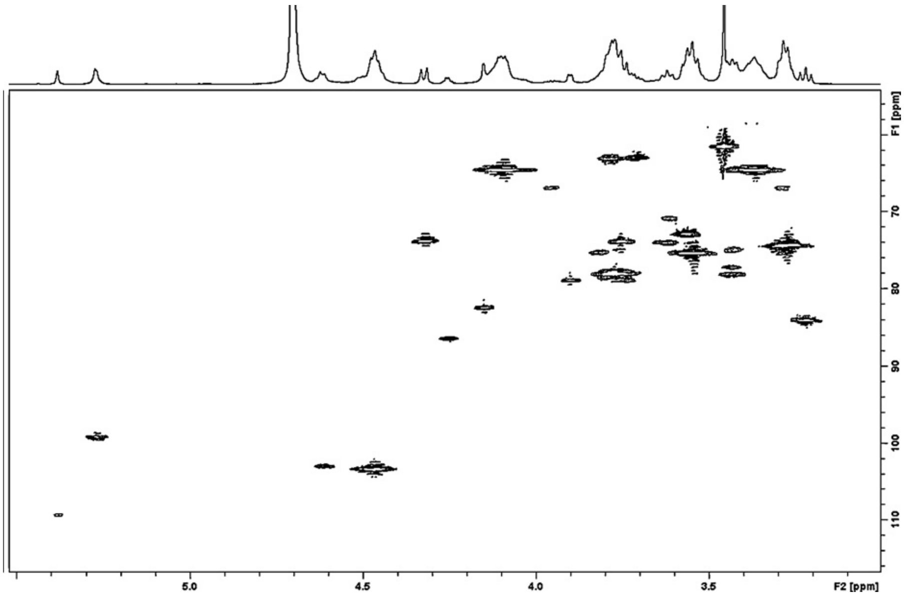

Fig. 1. ^{1}H–^{13}C HSQC NMR spectrum of AGX (27 °C, D_2O).

Table 1
^{1}H and ^{13}C NMR chemical shifts for AGX in D_2O at 27 °C.

			1	2	3	4	5e	5a	OMe
α-L-Ara*f*	A	^{1}H	5.384	4.152	3.908	4.257	3.784	3.716	
		^{13}C	109.25	82.4	78.9	86.4	62.9	62.9	
α-D-Glc*p*A	B	^{1}H	5.271	3.565	3.757	3.225	4.323	–	3.458
		^{13}C	99.07	72.96	73.9	84.12	73.7	–	61.4 C6 177.9
β-D-Xyl*p*	C	^{1}H	4.614	3.428	3.61	3.79	3.371	4.089	
		^{13}C	102.9	78.1	73.7	77.7	64.4	64.4	
β-D-Xyl*p*	D	^{1}H	4.505	3.425	3.743	3.813	3.328	4.044	
		^{13}C	103.1	74.2	78.0	75.2	64.4	64.4	
β-D-Xyl*p* free chain	E	^{1}H	4.4701	3.278	3.544	3.77	3.368	4.092	
		^{13}C	103.4	74.3	75.4	78.0	64.5	64.4	
β-D-Xyl*p*	F	^{1}H	4.458	3.281	3.557	3.767	a	a	
		^{13}C	[a]	[a]	[a]	[a]	[a]	[a]	
β-D-Xyl*p*	G	^{1}H	4.447	3.26	3.531	3.745	3.418	3.964	
		^{13}C	[a]	[a]	[a]	[a]	[a]	[a]	

[a] Not determined due to spectral overlap with the signals from sugar E.

chains on the main xylose chain was random or in blocks. However, the observation of NOE cross-peaks (at 300 ms mixing time) between H-1 of α-L-Ara*f* (A) and H-1 of β-D-Xyl (G) and between H-1 of 4-O-methyl-α-D-Glc*p*A (B) and H-1 of β-D-Xyl F (Table 2, Fig. 3) indicated that there is at least one free xylose on the main chain present between two substitutions (Fig. 4).

The integration of the anomeric protons of α-L-Araf-(1→3), 4-O-methyl-α-D-GlcpA and D-Xyl gave a 1:2:11 ratio. The ratio was in relatively good agreement with the dionex results, 21–27% substitution. Some additional minor peaks were observed in the NMR spectra but the intensities of these signals were too low to allow reliable assignments.

3.3. *SEC*

The spruce xylan was easily soluble in sodium nitrate. The light scattering (LS) shows two peaks (Fig. 5). The peak between 20 and 25 ml most likely represents the molecularly dissolved xylan and the peak at 15 and 20 ml most likely shows aggregated xylan. The refractive index (RI) detector is not recording the aggregated xylan which must be a quite minor quantity. The calculated weight average molecular weight (M_w) was 12,780 g/mol. The molecular weight recorded from the alkaline sodium hydroxide/acetate solution resulted in an average molecular weight of 11,200 g/mol. The two results show approximate

Table 2
Selected inter-residue NOESY from the anomeric protons.

Residue		H-1 δ_H (ppm)	Connectivities to: δ_H (ppm)	Inter-residue atom/residue
α-L-Ara*f*-(1→3)	A	5.384	3.743 (s)	H3 of D
			4.505 (m)	H1 of D
			4.447 (w)	H1 of G
4-OMe-α-D-Glc*p*A-(1→2)	B	5.271	3.428 (s)	H2 of C
			4.614 (m)	H1 of C
			4.458 (w)	H1 of F

(s) Strong NOE, (m) medium NOE, (w) weak NOE.

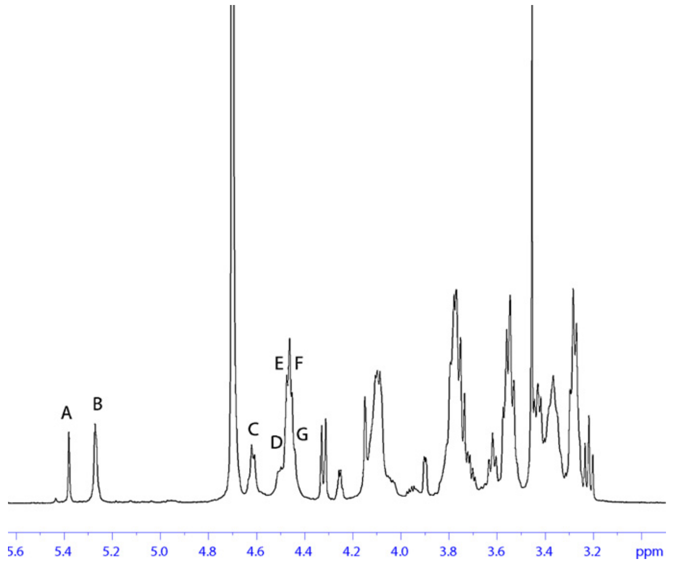

Fig. 2. ^{1}H NMR spectrum of spruce xylan showing corresponding major structural elements.

agreement with each other, when comparing the two analyses.

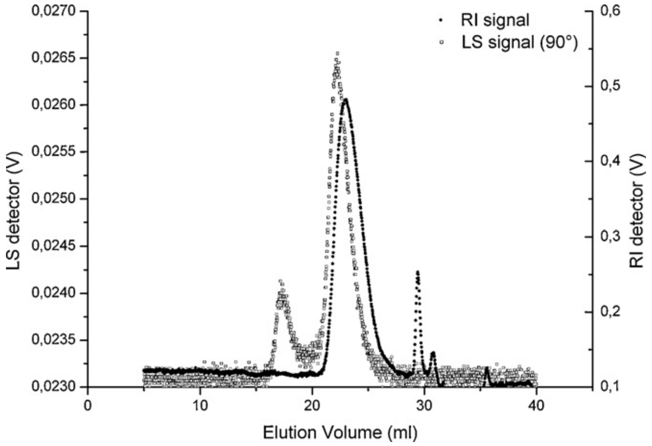

Fig. 5. Light scattering (LS) at 90° and refractive index (RI) signal of spruce xylan.

3.4. Material properties

Upon aqueous casting, arabinoglucuronoxylan formed transparent and homogeneous films without visible particles, easy to handle and of similar thickness, quite comparable to films prepared from barley husk arabinoxylans (Höije et al., 2005) and opposite to hardwood hemicelluloses (glucoronoxylan), which required plasticizers in order to form films (Gröndahl et al., 2004). The mechanical properties of the films were evaluated using tensile testing at 50% RH. Fig. 6 shows typical stress–strain curves for the arabinoglucuronoxylan films with various concentrations of sorbitol. The arabinoglucuronoxylan films were strong, with stress at break around 55 MPa, were quite flexible, with an elongation at break of around 2.7%; and were stiff, with Young's modulus of 2735 MPa, Table 3. Molecular weight of AGX along with its chemical structure, with arabinose and glucuronic acid pendant substituents, seem to allow for better mechanical properties of films made from this material as compared to films made from other hemicelluloses. For example arabinoxylans from barley husk had a M_w of around 36,000 and an arabinose content of 16%, with some of the xylan

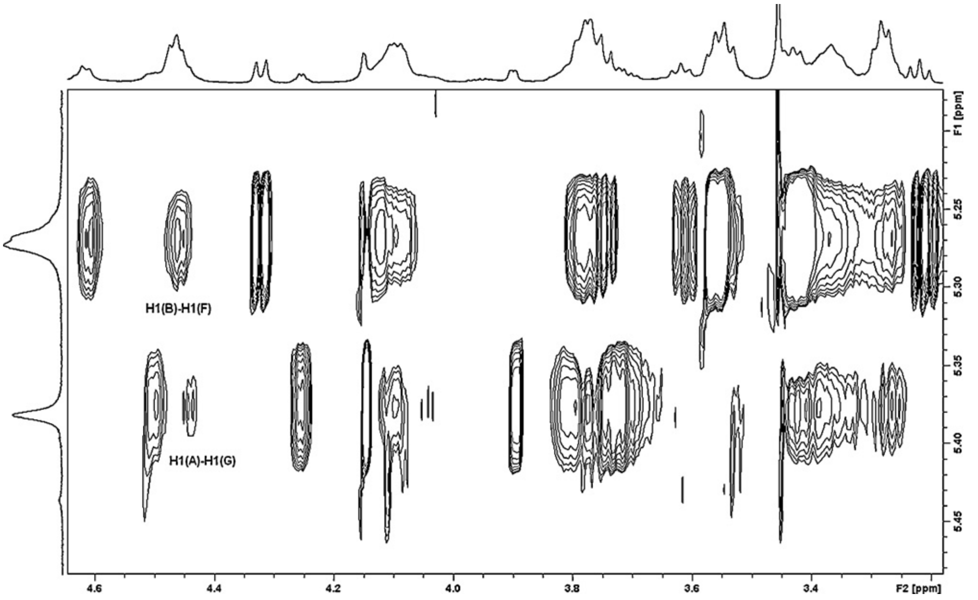

Fig. 3. Part of the 2D NMR NOESY spectrum of AGX showing NOEs cross-peaks from H-1 of A and H-1 of B (mixing time of 300 ms, 27 °C, D_2O). The non-sequential inter-residue NOEs are indicated.

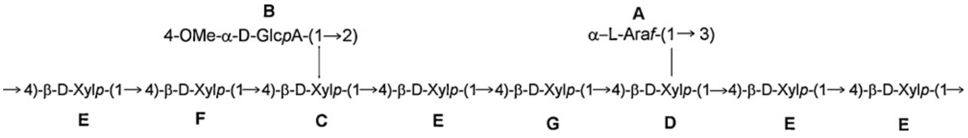

Fig. 4. Structural features of spruce xylan from ^{1}H and ^{13}C NMR analysis. A–G refers to NMR assignments.

Table 3
Tensile mechanical properties of AGX films.

Sample	Young's modulus (MPa)		Stress at break (MPa)		Strain at break (%)	
Control	2735	388	55	7	2.7	0.7
5%	2612	160	57	1	3.1	0.3
15%	2063	109	44	2	3.3	0.8
25%	1163	140	26	8	4.3	1.8

Table 4
Oxygen permeability of AGX films.

Material	Plasticizer	O_2 permeability ($cm^3\ \mu m\ m^2\ d^{-1}\ kPa^{-1}$)	Reference
Arabinoglucuronoxylan	–	0.12	Present study
Arabinoglucuronoxylan	Sorbitol 25%	0.17	Present study
Arabinoxylan	–	0.16	Gröndahl and Gatenholm (2007)
Glucuronoxylan	Sorbitol 35%	0.21	Gröndahl et al. (2004)
PVA	–	0.19	Sapalidis et al. (2007)

in a crystalline form, and their films had a stress at break above 50 MPa, elongation at break of around 2.5%, and Young's modulus of 2930 MPa (Höije et al., 2005). Films of AGX showed similar properties but with a lower molecular weight, a relatively low arabinose content and were completely amorphous (*vide infra*). On the other hand, glucuronoxylan from aspen had 83 wt.% xylose, 14 wt.% methyl glucuronic acid, 2 wt.% mannose, M_w 15,000, and their films with 20 wt.% plasticizer had a relative crystallinity of around 45%, and the mechanical properties can be compared to films made from pure AGX (Gröndahl et al., 2004). It appears that AGX hemicelluloses have the right balance between glucuronic acid and arabinose pendant groups and molecular weight that result in excellent material properties. Nonetheless, it is desirable to increase the strain of AGX films; however, addition of sorbitol at 5, 15 and 25% reduced the strength and the stiffness of the films but increased the flexibility, as expected.

Humidity scans in DMA were carried out at 25 °C and they show how the modulus of materials is influenced by air humidity. During the scan, the films gain water and become soft. The material softens at certain RH, which leads to a rapid decrease in the storage modulus, see Fig. 7. Water acts as a plasticizer and reduces the stiffness of the material. Plasticized arabinoglucuronoxylan films have a lower onset relative humidity. The plasticizers reduced the intermolecular interactions between the chains, thus facilitating interactions between water and hydroxyl groups of the glucuronic acid side group.

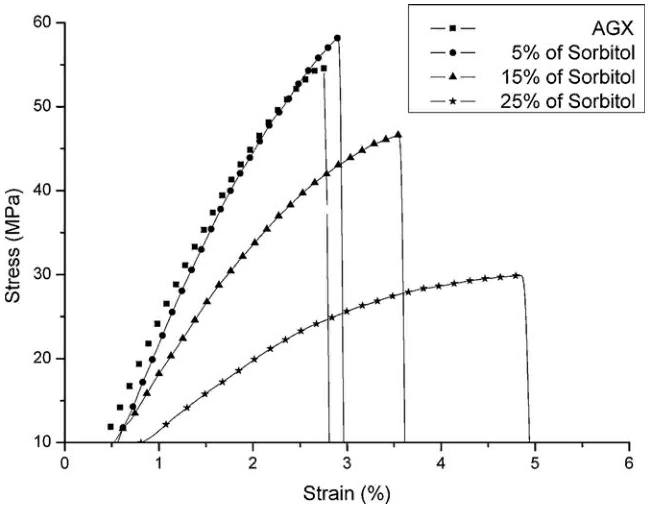

Fig. 6. Stress strain curve of spruce xylan film (AGX) and plasticized spruce xylan films at 25 °C and 50% RH.

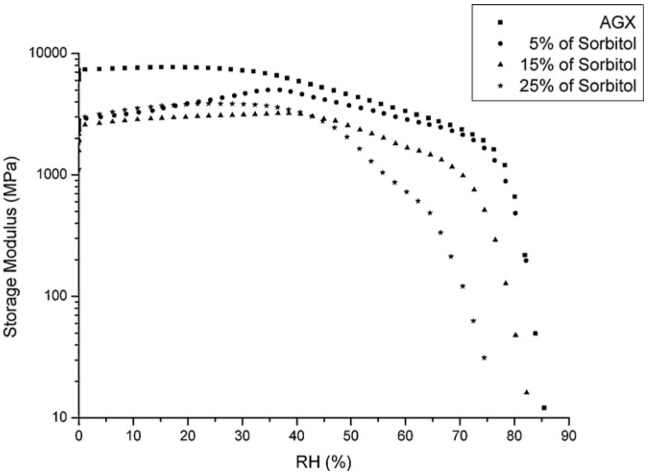

Fig. 7. DMA of spruce xylan (AGX) and plasticized spruce xylan films, humidity scans between 0 and 90%.

The morphology of the arabinoglucuronoxylan films was investigated using WAXS. The diffractograms showed that the AGX and the plasticized AGX are amorphous, see Fig. 8. Small crystalline peaks could be seen in the 15 and 25% plasticized films. These are most likely corresponding to crystalline sorbitol in distinct phase, and might have affected the plasticizing effect of sorbitol on the arabinoglucuronoxylan. Different humidity conditions, 30 and 70%, were evaluated when casting xylan films. The films were

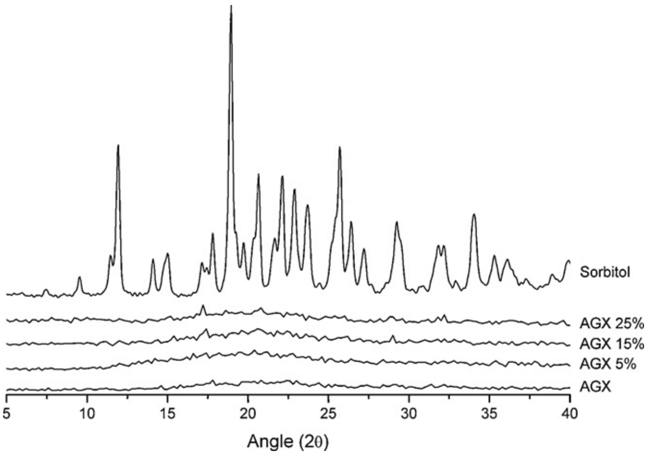

Fig. 8. X-ray diffractogram of spruce xylan films (AGX) and plasticized spruce xylan films.

amorphous and the relative humidity therefore did not seem to play a role in the crystallization during film formation.

Oxygen permeability of the arabinoglucuronoxylan film was measured at 50% RH. The average oxygen permeability was 0.12 (cm^3 μm m^{-2} d^{-1} kPa^{-1}). The measured oxygen permeability is slightly lower than previously reported data for glucuronoxylan and arabinoxylan films, see Table 4 (Gröndahl et al., 2004; Gröndahl & Gatenholm, 2007).

4. Conclusion

Highly purified arabinoglucuronoxylan can be extracted from Norway spruce in a yield between 7 and 10%. Structural features could be assigned to AGX based upon NMR analysis and SEC. Additional to carbohydrate analysis NMR showed that AGX has a ratio of 1:2:11 α-L-Araf-(1→3), 4-O-methyl-α-D-GlcpA and D-Xyl respectively.

The spruce xylan forms films without plasticizer which are clear, flexible and have great oxygen barrier properties.

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