

Films from Oat Spelt Arabinoxylan Plasticized with Glycerol and Sorbitol

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ABSTRACT: The development of packaging films based on renewable materials is an important and active area of research today. This is the first extensive study focusing on film-forming properties of an agrobiomass byproduct, namely, oat spelt arabinoxylan. A plasticizer was needed for cohesive film formation, and glycerol and sorbitol were compared. The tensile properties of the films varied with the type and amount of the polyol. With a 10% (w/w) plasticizer content, the films containing glycerol had higher tensile strength than the films containing sorbitol, but with a 40% plasticizer content, the result was the opposite. Sorbitol-plasticized films retained their tensile properties better than films with glycerol during 5 months of storage. The films were semicrystalline with similar crystallinity indices of 0.20–0.26. The largest crystallites (9.5 nm) were observed

in the film with 40% glycerol. The softening of films with 40% (w/w) glycerol started at a significantly lower relative humidity (RH) than that of the corresponding sorbitol-containing films. The films with sorbitol also had lower water vapor permeability (WVP) than the films with glycerol. The films plasticized with 10% (w/w) sorbitol had a WVP value of 1.1 g mm/(m²·d·kPa) at the RH gradient of 0/54%. The oxygen permeability of films containing 10% (w/w) glycerol or sorbitol was similar: 3 cm³·μm/(m²·d·kPa) at 50–75% RH. A higher plasticizer content resulted in more permeable films. Permeation of sunflower oil through the films was not detected. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 457–466, 2009

Key words: crystal structures; films; mechanical properties

INTRODUCTION

Oat (*Avena sativa*) spelts, composing almost 40% of the grain total weight, are the major byproduct of oat milling. They are mainly used as a low-value animal feed additive.¹ Recent research has been aimed at the isolation and utilization of arabinoxylan (AX), a polysaccharide constituting 35–40% of oat spelts, and thus at obtaining value-added products from this agrobiomass byproduct.^{2–4}

Cereal AXs consist of 1,4-linked β-D-xylopyranosyl backbones to which groups of α-L-arabinofuranosyl units are connected by 1,3- and/or 1,2-glycosidic linkages at irregular intervals. Many AXs also carry 4-O-methyl-α-D-glucopyranosyluronic acid and esterified side groups, mainly acetyl and feruloyl groups.^{5,6} The apparent molar mass of oat spelt ara-

binoxylan (osAX) has been reported to vary between 50 and 170 kDa.⁷

Xylans from both agricultural and wood sources have been studied as edible or biodegradable film formers. Barley (*Hordeum vulgare*), wheat (*Triticum aestivum*), rye (*Secale cereale*), and corn (*Zea mays*) AXs have been reported to form cohesive films from an aqueous solution.^{8–11} A combination of aspen (*Populus tremula*) glucuronoxylan and chitosan resulted in self-supporting films.^{12,13} The formation and homogeneity of films from corn AX esters blended with cellulose ester have also been tested.¹⁴ In many cases, polyols have been added as plasticizers to enhance the mechanical properties of xylan films. The use of glycerol and sorbitol has been successful, but xylitol crystallized in aspen glucuronoxylan-based films.^{15–18}

The mechanical, thermal, and barrier properties of edible or biodegradable films determine their applicability as protective coatings or packages. The tensile strength and elongation at break (EB) of previously studied xylan films varied from less than 1 MPa and almost 90%, respectively, for glycerol-plasticized films from cotton (*Gossypium hirsutum*) stalk xylan¹⁸ to 50 MPa and 2.5% for films from barley AX prepared without the addition of a plasticizer.⁸ The intermediate tensile strength and EB were obtained

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when corn AX films were plasticized with glycerol or sorbitol at a concentration of approximately 30% (w/w of total dry weight).¹⁷ Birch (*Betula*) xylan mixed with wheat gluten produced films with a tensile strength similar to that of pure gluten-based films but with decreased EB.¹⁹ Xylan films were found to be sensitive to high ambient relative humidity (RH).^{10,11,16} The use of glycerol further increased the water vapor transmission rate (WVTR) of xylan films.¹⁸ Increased hydrophobicity of AX films was sought by chemical modifications and emulsification of lipids into the film matrix.^{15,20–24} Aspen glucuronoxylan and barley AX films showed potential as oxygen barriers.^{16,25} Extensive studies of osAX-based films have not been published previously. The aim of this study was to examine the film-forming capacity of osAX, to evaluate the morphology and properties of the films from a food application perspective, and to compare the actions of glycerol and sorbitol as external plasticizers of osAX films.

EXPERIMENTAL

Materials

The osAX (CAS 9014-63-5) was purchased from Sigma–Aldrich (St. Louis, MO). Glycerol, xylitol, and sorbitol were acquired from BDH Laboratory Supplies (Lutterworth, England), Danisco (Kotka, Finland), and Cerestar (Krefeld, Germany), respectively. NaCl, NaAc, Mg(NO₃)₂, NaNO₂, KCl, and anhydrous CaCl₂ with a granular size of 1–2 mm were obtained from Merck (Whitehouse Station, NJ). The sunflower oil (Raisio Oyj, Raisio, Finland) was purchased from a grocery store.

Preparation of the films

A suspension was made from osAX in deionized water (14 g/L weighed on an as-is basis) and mixed by magnetic stirring at 90–95°C for 15 min. The suspension was centrifuged at 17,000 rpm (22,500 g) for 15 min, and the insoluble part (4 g/L) was removed. The monosaccharide composition of the untreated osAX and the liquid part after centrifugation were determined by gas chromatography (HP 5890 series II, Hewlett–Packard, Palo Alto, CA)²⁶ after acid methanolysis.²⁷ A supernatant containing 10 g/L osAX was taken for film preparation. When used, glycerol or sorbitol was added as a plasticizer, and the solution was heated to 60–70°C under magnetic stirring to enhance their dissolution and even distribution. The solution was degassed by ultrasonication *in vacuo* for 5 min, after which it was cast into polystyrene Petri dishes. The thickness of the films was adjusted by the solution volume, which was 125 mL

in a 14-cm-diameter dish for dynamic mechanical analysis (DMA; film thickness \approx 100 μ m), 100 mL in a 14-cm-diameter dish for studying the effect of salt (film thickness \approx 80 μ m), 100 mL in a 9-cm-diameter dish for crystallinity measurements (film thickness \approx 190 μ m), and 50 mL in a 14-cm-diameter dish for all other tests (average film thickness = 20–50 μ m). The films were dried in a climate room at 23°C and 50% RH for 3 days and then aged under these conditions for at least 7 days before the analysis, except when the effect of aging on the film properties was studied; then, the films were dried at 60°C for 4 h and subsequently stored in the climate room (50% RH) between printing papers for 7–169 days. To study the effect of salt on the mechanical properties of the films, 5 or 10% (w/w of osAX) NaCl and NaOAc were dissolved in the centrifuged supernatant, after which sorbitol (40% w/w of osAX) was added as a plasticizer, and the preparation of the films was continued as described previously. Testing of the tensile strength and EB was performed on all cohesive films obtained. Grease permeability was studied on films plasticized with 40% (w/w of osAX) glycerol or sorbitol. Other analyses were done of films plasticized with 10 or 40% glycerol or sorbitol.

Tensile testing

The tensile strength, EB, and Young's modulus of the films were determined at 23°C and 50% RH with an Instron 4465 universal testing machine (Instron Corp., High Wycombe, England) with a load cell of 100 N. The initial grip distance was 50 mm, and the rate of grip separation was 5 mm/min. The specimen width was 10 mm, and the length was approximately 100 mm. The thickness of the specimens was measured with a micrometer (Lorentzen & Wettre, Kista, Sweden; precision = 1 μ m) at five points, and an average was calculated. When continuous films were formed, 6–12 replicate specimens of each film type were measured.

DMA

The α -relaxation [glass-transition temperature (T_g)] of films was studied with temperature scans taken with a dynamic mechanical analyzer (DMA 242, Netzsch-Gerätebau GmbH, Selb, Germany). Three conditioned specimens (10 \times 50 mm²) were analyzed with a dual-bending sample holder with a free bending length of 18 mm. The storage modulus (E') and loss modulus (E'') data were collected at a heating rate of 2°C/min from –120 to 50°C at frequencies of 1, 2.5, 5, 10, and 20 Hz. T_g was taken as the peak temperature of E'' at 1 Hz,²⁸ which was determined through the fitting of a parabolic curve to the E'' data with Origin 7.2 software (OriginLab Corp.,

Northampton, MA). The average of three thickness measurements, taken with a Mitutoyo micrometer (Mitutoyo Corp., Kanagawa, Japan; precision = 10 μm), was determined for each specimen.

Humidity scans were performed on a PerkinElmer (Waltham, MA) DMA 7e. An amplitude of 5 μm for films containing 10% glycerol or sorbitol or 10 μm for films containing 40% glycerol or sorbitol was applied to the specimens at a frequency of 1 Hz. The E' data were collected while the RH was increased from 1 to 90% at a rate of 0.1%/min. The temperature was maintained at 30°C. The specimen width was 5 mm, and the clamp distance was approximately 12 mm.

Thermogravimetric analysis

A Mettler–Toledo TGA 850 thermogravimetric analyzer (Mettler–Toledo, Inc., Greifensee, Switzerland) equipped with STAR^e software (Star Software Systems Corp., Warner Robins, GA) was used to determine the water content of the films conditioned in the climate room. Three replicate specimens of each film were heated from 25 to 120°C at a heating rate of 50°C/min. The temperature was then maintained at 120°C for 10 min, during which a steady specimen weight was reached. The weight loss during the heat treatment was taken as the water content.

X-ray diffraction (XRD)

The XRD pattern of the film plasticized with 10% glycerol was measured with both the symmetrical transmission and symmetrical reflection geometry to study the crystallinity and preferred orientation of the crystallites in the film. The measurement setup consisted of a sealed copper-anode X-ray tube, a four-circle goniometer (J. M. Huber Corp., Rimsting, Germany), and a scintillation detector (Quartz & Silice, Nemours, France). The wavelength of the X-ray beam was 1.5408 Å, and it was selected with a bent and cut germanium monochromator (J. M. Huber). The measurements were made with scattering angles of 5–60° with continuous rotation of the film around the axis normal to the plane of the film. Only one sample was measured with this setup because of the very long measurement times required (several days for each measurement).

Films plasticized with 10 or 40% glycerol or sorbitol were measured with another XRD setup with perpendicular transmission geometry. The measurement setup consisted of a sealed copper-anode X-ray tube, a multilayer monochromator (Incoatec, Hamburg, Germany), and an image plate detector (MAR345, Mar Research, Norderstedt, Germany). Cu K α radiation with a wavelength of 1.542 Å was used. Calibration of the 2 θ scale was performed by

the measurement of the diffraction patterns of the silver behenate ($\text{AgC}_{22}\text{H}_{43}\text{O}_2$) and silicon powder samples. The measurement time was 1 h for each sample.

The diffraction patterns were corrected for air scattering, sample absorption, and detector geometry. For these corrections, the transmission of the X-ray beam through the films was determined from the image of the beam on the detector after a semi-transparent beam stop, and the thickness of the films was determined with a digital micrometer (MDC-25SB, Mitutoyo, Kawasaki, Japan; accuracy = 2 μm). The crystallinity index (ϕ) of the samples was calculated by the determination of the ratio of the intensity of the amorphous regions ($I_{\text{amorphous}}$) to the total intensity ($I_{\text{experimental}}$) of the film with the following formula:

$$\phi = 1 - \frac{\sum I_{\text{amorphous}}}{\sum I_{\text{experimental}}} \quad (1)$$

The amorphous background ($I_{\text{amorphous}}$) was obtained through the fitting of the amorphous model (a polynomial of 6°) and the crystalline model (consisting of 44 reflections of xylan dihydrate)²⁹ to the experimental diffraction pattern within a scattering angle (2 θ) range of 6–44°. The data analysis was carried out with the program MATLAB (The Mathworks, Inc., Natick, MA). The accuracy of ϕ was estimated to be 0.05.

Water vapor permeability (WVP)

Melted paraffin wax was used to seal the films on aluminum cups ($\phi 80$ mm) containing 30 g of CaCl_2 as a desiccant. The air gap between the desiccant and the underside of the film was approximately 6 mm. The cups were placed in a desiccator cabinet in which the air velocity above the samples was 0.15 m/s. The cabinet was kept at 22°C, and its RH was maintained at 54%, 66%, and 86% with saturated $\text{Mg}(\text{NO}_3)_2$, NaNO_2 , and KCl solutions, respectively. The cups were weighed four to seven times at intervals of 1–24 h. The temperature and RH of the cabinet were measured before each weighing with a Rotronic (Bassersdorf, Switzerland) Hygro-Palm RH meter. The WVTR was calculated from a linear regression of the slope of the weight gain versus time by division of the slope by the test cell mouth area. The water vapor partial pressure at the underside of the film was calculated with the correction method described by Gennadios et al.³⁰ The WVP was obtained by multiplication of the WVTR by the thickness of the film and division by the water vapor partial pressure difference between the two sides of the film. Three replicates of each film

type were tested, and their thickness was measured before testing at 10 points with 1- μm precision.

Oxygen permeability (OP)

The oxygen gas transmission rate (OTR) of the films was measured with an OP tester with a coulometric sensor (Ox-Tran Twin, Modern Controls, Inc., Minneapolis, MN). The specimens were placed in the instrument for approximately 20 h before testing to condition them to the RH inside the test cells, which was reported in the instrument manual to be 50–75%. The film was exposed to 100% oxygen on one side and to a mixture of 98% nitrogen and 2% hydrogen on the other side. The OP was calculated by multiplication of the OTR with the thickness of the film and division by the oxygen gas partial pressure difference between the two sides of the film. The measurement was carried out at 22°C and normal atmospheric pressure. The specimen area was 5 cm², and the thickness of the film was measured after analysis at five points with a micrometer with 1- μm precision. The OP was determined for four replicates from each film.

Grease permeability

A film specimen of approximately 40 cm² was placed on a ground glass plate, and two pieces of thin fiber cloth with a weight of 16 g/cm² were set on top of the film. The system was stabilized at 60°C for 30 min, after which 500 μL of sunflower oil was added to the cloth. The migration of oil on the glass surface at 60°C was examined visually every 30 min for the first 2 h and later at convenient intervals. The grease permeability was followed for 48 h for two replicate specimens of each film.

Principal component analysis (PCA)

The average results of the tensile strength, EB, Young's modulus, T_g , water content, lattice constants a and c , ϕ , WVP at a gradient of 0–54% RH, and OP of the films plasticized with 10 or 40% glycerol or sorbitol were examined with PCA. SPSS 15.0 (SPSS, Inc., Chicago, IL) was used.

RESULTS AND DISCUSSION

Film formation and tensile properties

The film preparation was first tested through the casting and drying of the plasticized osAX suspension. The obtained films were heterogeneous, discontinuous, and weak. Cohesive films were formed, and the appearance of the films greatly improved when the main insoluble part was removed. Gas chromatography analysis showed that the xylose/arabi-

nose/glucose weight ratio of osAX was 84 : 8 : 8, whereas after centrifugation it was 83 : 12 : 5. The insoluble part thus appeared to contain xylan less substituted with arabinose and a glucan such as cellulose.

Even when the insoluble part was removed, osAX did not form self-supporting films without an external polyol plasticizer, unlike AXs from barley, wheat, rye, and corn, which contain more arabinose substituents and are more soluble in water than osAX.^{8–11} In preliminary experiments, glycerol, sorbitol, and xylitol were tested in various amounts and as binary mixtures. A decrease in the tensile strength and an increase in EB were seen when the amounts of the polyols were increased, as expected.³¹ Migration and/or crystallization of xylitol (but not of glycerol, sorbitol, or the polyol mixtures) on the film surface was visually observed. Using polyol mixtures did not have a notable effect on the tensile properties of the films, and so pure glycerol and sorbitol were selected for further experiments. All films obtained were easy to handle and were of similar thickness, regardless of the plasticizer content.

When 10% polyol was used, the films containing glycerol had a higher tensile strength than those containing sorbitol [Fig. 1(A)]. With a polyol content of 40%, the result was contrasting, so the sorbitol-plasticized films were somewhat stronger than the glycerol-plasticized films. There was no clear difference between the EB of films plasticized with glycerol or sorbitol [Fig. 1(B)], but in the Young's modulus results, a trend similar to that for the tensile strength was seen [Fig. 1(C)]. The tensile properties of osAX films containing 10% glycerol were comparable to those reported earlier for corn AX films plasticized with 15–20% glycerol (w/w of solids), but the previously studied sorbitol-plasticized corn AX films had higher tensile strength than osAX-sorbitol films.^{15,17}

Dynamic mechanical properties

The temperature-scan DMA spectra were similar to those reported previously for galactomannan-based films.³² A decrease in E' and a peak in E'' were detected as indications of the T_g values of the films. The T_g values supported the results of the tensile testing. The films containing 10% glycerol had a T_g value of 17°C (Table I); thus, at the temperature used for tensile testing (23°C), the films were close to their glass transition. This explains the higher tensile strength and Young's modulus of the films plasticized with 10% glycerol versus the films plasticized with 10% sorbitol (Fig. 1), the T_g values of which were lower (Table I). At low contents, glycerol may induce an antiplasticization effect, which is a known

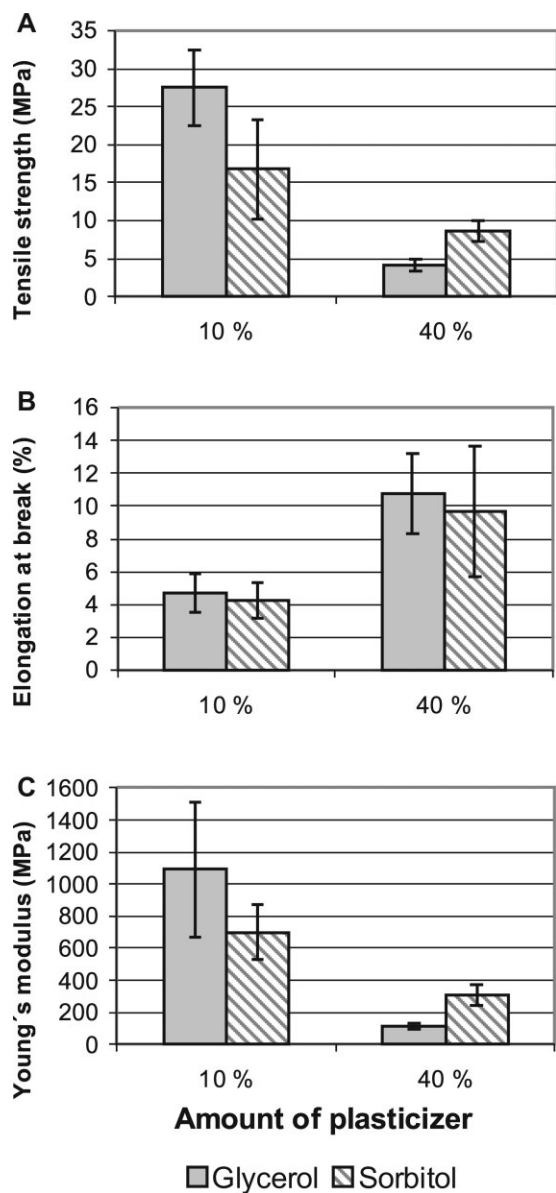


Figure 1 (A) Tensile strength, (B) EB, and (C) Young's modulus of films plasticized with 10 or 40% (w/w of osAX) glycerol or sorbitol. The averages were based on 11 or 12 measurements, and the error bars indicate standard deviation.

phenomenon for synthetic polymers and has also been studied with starch–glycerol films.³³ Antiplasticization leads to increased tensile strength, decreased EB, and high T_g values at low plasticizer contents. However, the detailed mechanisms involved are not well known.

When plasticized with 40% polyol, the films containing glycerol had lower T_g values than those containing sorbitol. This, together with the results from tensile testing, indicates that at high contents, glycerol was a more effective plasticizer of osAX films than sorbitol. The T_g values did not correlate with the water contents of the films (Table I). At the 10% polyol level, the water contents of films plasticized

TABLE I
 T_g 's and Water Contents of the Films Conditioned at 50% RH (Mean \pm Standard Deviation from at Least Three Measurements)

Plasticizer (w/w of osAX)	T_g ($^{\circ}$ C)	Water content (% w/w)
10% glycerol	17 \pm 6	11.2 \pm 0.5
10% sorbitol	-10 \pm 1	11.1 \pm 0.2
40% glycerol	-59 \pm 6	12.5 \pm 0.9
40% sorbitol	-24 \pm 11	10.4 \pm 0.9

with glycerol or sorbitol did not differ significantly. In contrast, increasing the polyol content to 40% increased the water content of glycerol-plasticized films but decreased that of sorbitol-plasticized films.

After an initial increase in E' of some films at low RH levels, which could be explained by an antiplasticizing effect of water,³⁴ E' of all studied films decreased with increasing RH (Fig. 2). Remarkable effects of the amount and type of the polyol were seen because the greatest E' decrease occurred in different RH regions depending on the film composition. Softening of the film plasticized with 40% glycerol started at a considerably lower RH than that of the other films studied. At about 30% RH, E' of the film containing 40% glycerol decreased to half of its E' value at 0% RH. The film plasticized with 40% sorbitol showed a steep drop in E' between RH levels of 40 and 60%. With a polyol content of 10%, the differences in E' between glycerol- and sorbitol-plasticized films were relatively small, and the decrease in E' of these films occurred within a wide RH range. The relative E' values of films containing 10% glycerol or sorbitol decreased to 50% at 65–70% RH. The results are in agreement with previous studies indicating the softening effects of water on xylan films^{11,16} and the softening of glycerol-plasticized spruce galactoglucomannan films at lower RHs in comparison with sorbitol-containing films,³⁵ and they suggest that the interaction effect of polyol

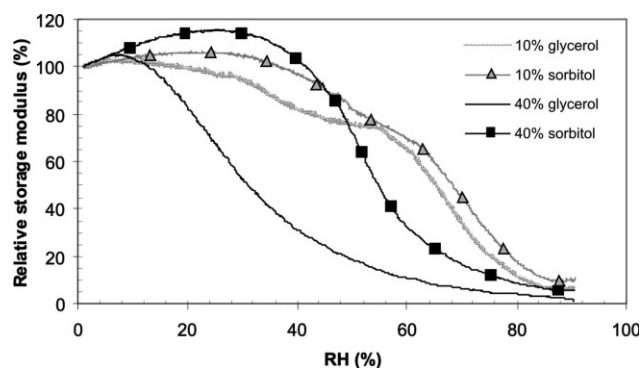


Figure 2 Effect of RH on E' of the films.

TABLE II
***a* and *c* Values for the Films and ϕ Determined by XRD**

Plasticizer	<i>a</i> (Å)	<i>c</i> (Å)	ϕ
10% glycerol	9.58 ± 0.01	15.21 ± 0.08	0.23 ± 0.05
10% sorbitol	9.33 ± 0.01	15.56 ± 0.08	0.20 ± 0.05
40% glycerol	9.79 ± 0.01	15.06 ± 0.08	0.26 ± 0.05
40% sorbitol	9.66 ± 0.01	15.23 ± 0.08	0.22 ± 0.05

and water should be considered in developing film applications.

Morphology of the films

The osAX films were semicrystalline, and ϕ was between 0.20 and 0.26 (Table II). The values were almost equal if we take into account the accuracy of the determination (5%). The two-dimensional XRD of the film plasticized with 10% glycerol showed isotropic Debye rings. From this, it can be concluded that the crystallites were randomly oriented in the plane of the films. However, the xylan chains in the crystallites were oriented preferably parallel to the surface of the film. This preferred orientation of the crystallites was revealed by a comparison of diffraction patterns measured by symmetrical reflection and transmission geometry. The XRD patterns of films with 10 or 40% glycerol or sorbitol measured in perpendicular transmission geometry are shown in Figure 3. The positions of the diffraction peaks

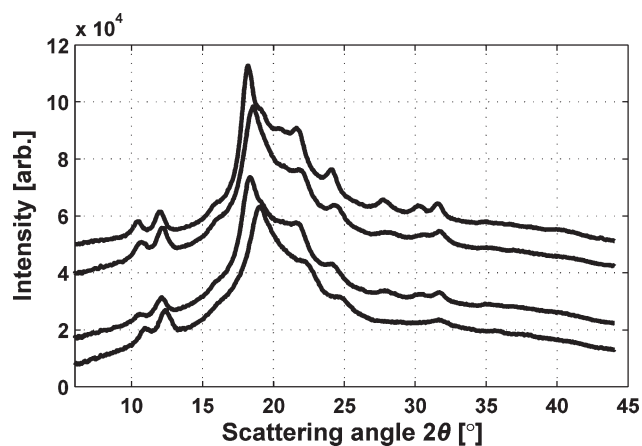


Figure 3 XRD patterns of the films measured with perpendicular transmission geometry. Plasticizer content from bottom to top: 10% sorbitol, 40% sorbitol, 10% glycerol, and 40% glycerol. The intensity scales were shifted for clarity.

were in agreement with a hexagonal crystal structure. However, the positions of the diffraction peaks as well as the lattice constants differed slightly from those determined for xylan dihydrate ($a = 9.64$ Å and $c = 14.95$ Å;²⁹ Fig. 4). The lattice constants are given in Table II. In all cases, c was larger than that determined by Nieduszynski and Marchessault.²⁹

The unit cell was narrower in the direction perpendicular to the xylan chains in films with 10% plasticizer versus those with 40% plasticizer. This is

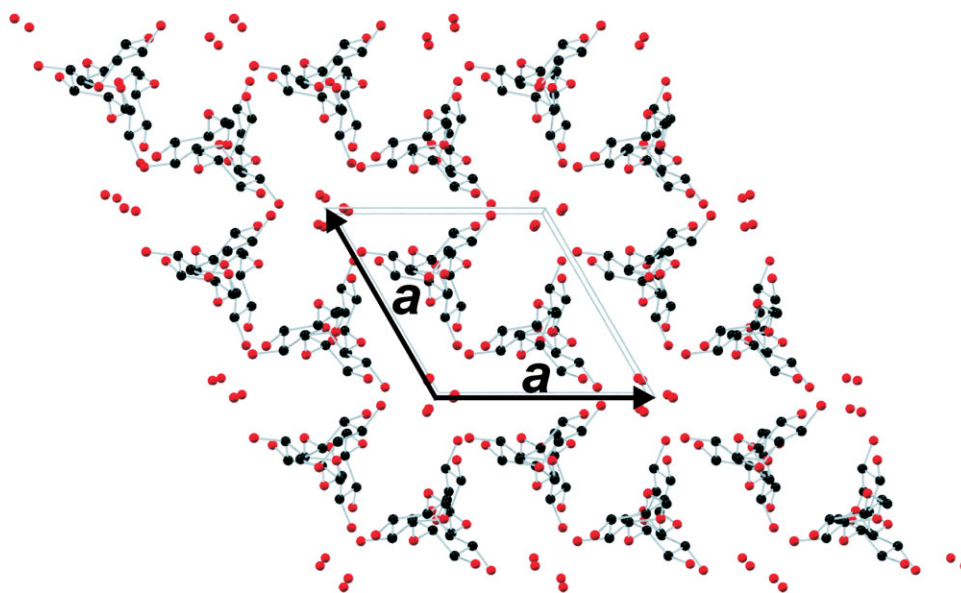


Figure 4 Crystalline structure of xylan dihydrate, illustrated according to the data by Nieduszynski and Marchessault.²⁹ The black parallelepiped shows the unit cell. In total, nine unit cells are shown. The c axis is perpendicular to the plane of paper. In the hexagonal structure, lattice vectors \mathbf{a} and \mathbf{b} are of the same length. The black and red spheres denote the carbon and oxygen atoms, respectively. Hydrogen atoms are not shown. The groups of oxygen atoms between the xylan chains correspond to water molecules within the structure. The figure was prepared with the programs PowderCell 2.4 (Federal Institute for Materials Research and Testing, BAM, Berlin, Germany) and POV-Ray 3.6. (Persistence of Vision Raytracer, Pty. Ltd., Williamstown, Australia). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE III
WVTR, WVP, and Corrected WVP³⁰ of the Films at Different RH Gradients and at 22°C (Mean ± Standard Deviation from Three Measurements)

RH gradient (%)	Plasticizer	WVTR (g m ⁻² × d ⁻¹)	WVP (g mm × m ⁻² × d ⁻¹ · kPa ⁻¹)	Corrected WVP (g mm × m ⁻² × d ⁻¹ · kPa ⁻¹)
0/54	10% glycerol	180 ± 5	3.2 ± 0.2	3.3 ± 0.2
0/54	10% sorbitol	70 ± 16	1.1 ± 0.1	1.1 ± 0.1
0/54	40% glycerol	580 ± 34	11 ± 2	13 ± 3
0/54	40% sorbitol	90 ± 10	1.8 ± 0.2	1.9 ± 0.2
0/66	10% glycerol	840 ± 22	9.4 ± 1	11 ± 1
0/66	10% sorbitol	430 ± 82	4.5 ± 0.3	4.9 ± 0.4
0/66	40% glycerol	1800 ± 89	30 ± 4	49 ± 8
0/66	40% sorbitol	690 ± 110	10 ± 0.7	12 ± 0.6
0/86	10% glycerol	2370 ± 68	25 ± 2	41 ± 4
0/86	10% sorbitol	1800 ± 79	19 ± 3	26 ± 3
0/86	40% glycerol	2900 ± 190	41 ± 4	78 ± 12
0/86	40% sorbitol	2050 ± 34	24 ± 5	36 ± 7

in agreement with the results presented by Gröndahl et al.¹⁶ on aspen wood glucuronoxylan films plasticized with xylitol or sorbitol. The polyol could interact and even cocrystallize with xylan. However, because the changes in the lattice constant were not large, we suggest that these changes were caused by different degrees of hydration.

The films with 10 and 40% polyol exhibited crystallites of a size of 76–81 ± 1 and 87–95 ± 1 Å perpendicular to the xylan chains, respectively. These values were obtained from the full width at half-maximum of the 100 reflection with the Scherrer formula³⁶ with instrumental broadening of 0.23°. The largest crystallites were observed in the film with 40% glycerol, which also showed the highest crystallinity. It has been suggested that plasticization may increase the crystallinity of the film by increasing the polymer chain mobility.^{16,37} The association between the crystalline structure and the mechanical and barrier properties of xylan films will be a subject of further studies.

Permeability properties

Susceptibility to moisture and its relation to the type and amount of the polyol were also clearly seen in the WVP results. The WVP notably increased with the RH gradient and polyol content increasing (Table III). The WVP of the sorbitol-plasticized films was lower than that of the corresponding glycerol-plasticized films, and the films containing 10% sorbitol had the lowest WVP in all three studied RH gradients. Interestingly, the WVP of films plasticized with 40% sorbitol was rather similar to that of films plasticized with 10% glycerol in each RH gradient. In agreement with the humidity-scan DMA results, the WVP measurements showed that the films plasticized with 40% glycerol were the most sensitive to changes in RH because they had the greatest increase in WVP with the RH gradient increasing. The films

with the highest WVP, plasticized with 40% glycerol, also had the highest water content (Table I), but the level of WVP of the films with the lowest water content, plasticized with 40% sorbitol, was intermediate. In comparison with many previously studied biodegradable films, the WVP values obtained here are higher,³⁸ but they are similar to those reported for corn AX films with low polyol contents.^{15,17}

The OP of films containing 10% glycerol or sorbitol was similar (Table IV). With a polyol content of 40%, sorbitol resulted in more effective oxygen barrier films than glycerol. In comparison with films from other biopolymers and synthetic materials, the OP of osAX films was low,³⁷ but it was not as low as that reported for the widely used oxygen barrier ethylene vinyl alcohol or for films from aspen glucuronoxylan and barley AX.^{16,25} In addition to WVP and OP, the grease permeability of the films was studied. Permeation of sunflower oil through osAX films was not detected during a period of 48 h at 60°C.

PCA

PCA was used as an explanatory tool for grouping the measured variables and visualizing the positions of different film types with respect to their properties (Fig. 5). The first two principal components (PC1 and PC2) explained 74.2% and 16.4% of the variance,

TABLE IV
OTR and OP of the Films at 50–75% RH and at 22°C (Mean ± Standard Deviation from Four Measurements)

Plasticizer	OTR (cm ³ m ⁻² × d ⁻¹)	OP (cm ³ μm m ⁻² × d ⁻¹ · kPa ⁻¹)
10% glycerol	10.7 ± 0.9	3.0 ± 0.9
10% sorbitol	12.5 ± 2.7	3.2 ± 0.6
40% glycerol	15.9 ± 4.4	7.4 ± 0.5 ^a
40% sorbitol	9.6 ± 1.8	4.7 ± 1.6

^a Only three measurements.

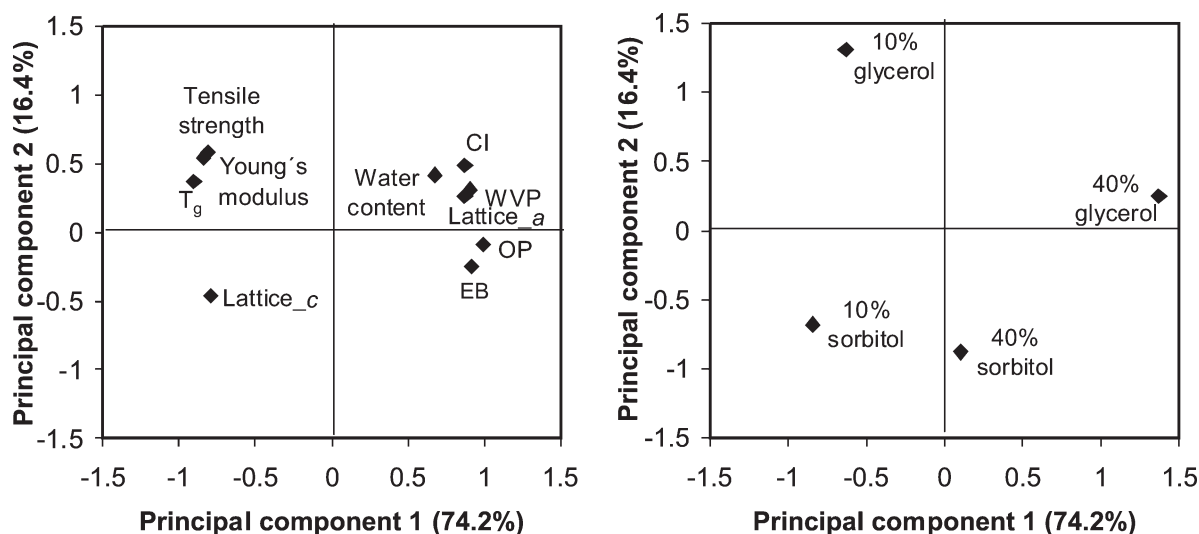


Figure 5 (A) PCA factor loadings for the film properties and (B) factor scores for the film types plotted against the first two principal components (lattice_a = *a*; lattice_c = *c*; CI = crystal index).

respectively, and resulted in a cumulative value of 90.6%. The variables with high PC1 loadings were associated with a high level of plasticization and molecular mobility in the films. These variables included the water content, ϕ , WVP, *a*, OP, and EB. Variables associated with a low level of plasticization and low PC1 loadings were the tensile strength, Young's modulus, T_g , and *c*. High levels of PC2 loading tended to follow plasticization by glycerol, although this was not straightforward because some variables reached both the maximum and minimum values with plasticization by glycerol in different amounts. PCA supported the conclusion that the properties of osAX films can be strongly affected by the variation of the amount and type of the plasticizer.

Effect of salt

Technical xylan preparations may contain impurities such as salts, the effect of which on film properties is not known. In this study, the addition of NaAc or NaCl decreased the tensile strength of the films [Fig. 6(A)]. Either salt even at a concentration of only 5% (w/w of osAX) had a notable effect. Differences in the EB values of the films were smaller and can be explained by high standard deviations [Fig. 6(B)]. However, the results suggest that the purity of isolated AX preparations should be carefully controlled because salt residues can interfere with xylan film formation and reduce the mechanical durability of the film.

Effect of the storage time

The tensile properties of films plasticized with 40% glycerol or sorbitol and stored between printing

papers at 23°C and 50% RH were followed monthly for 5 months (Fig. 7). The glycerol-plasticized films showed a significant increase in the tensile strength

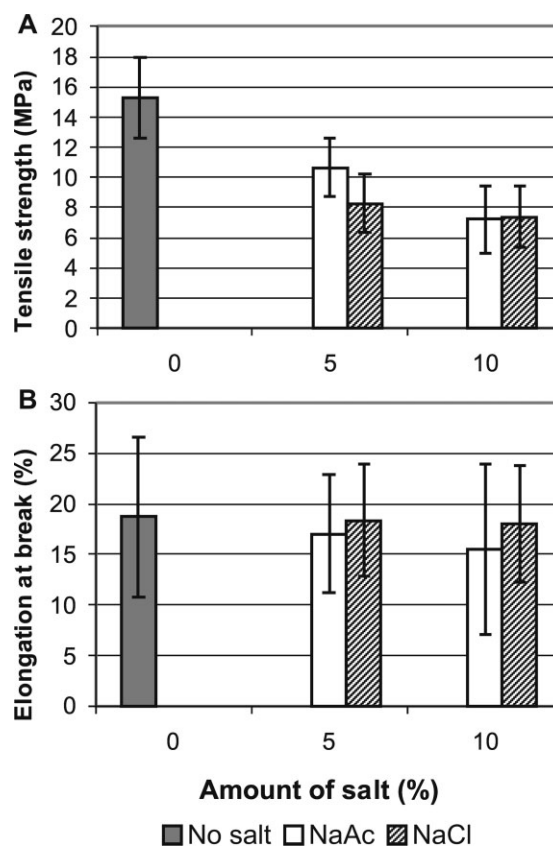


Figure 6 Effect of NaAc and NaCl (w/w of osAX) on the (A) tensile strength and (B) EB of films plasticized with 40% (w/w of osAX) sorbitol. The averages were based on six to nine measurements, and the error bars indicate standard deviation.

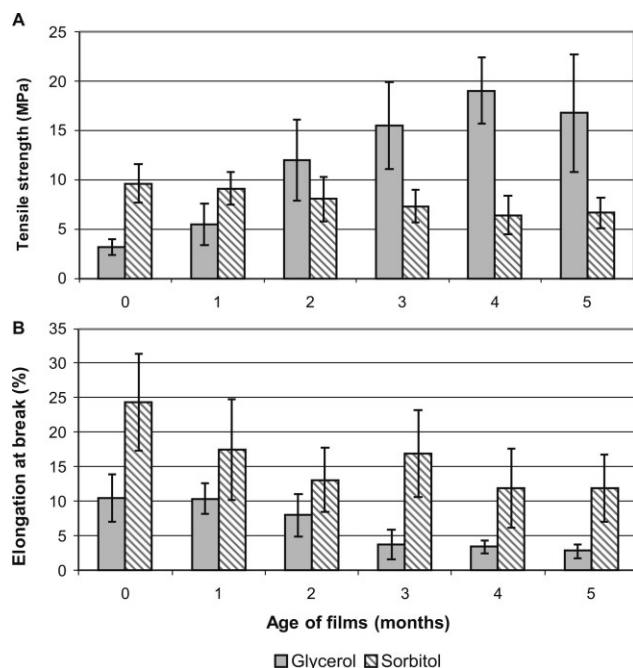


Figure 7 Effect of the storage time on the (A) tensile strength and (B) elongation of films plasticized with 40% (w/w of osAX) glycerol or sorbitol. The averages were based on 8–12 measurements, and the error bars indicate standard deviation.

during this time, and concomitantly, EB decreased. The results suggest that the migration of glycerol from the film matrix occurred, resulting in decreased plasticization of the films. The effect of the storage time on the tensile properties of sorbitol-plasticized films was not quite as significant as that for glycerol-plasticized films. The tensile strength of films containing sorbitol slightly decreased during the observation time. EB of sorbitol-plasticized films also showed a tendency to decrease. There was a decrease in EB of sorbitol-plasticized films after 2 months, but this could be explained by high experimental variation, which is typical for laboratory-prepared biopolymer films and can originate from heterogeneity of the starting material or differences in film thickness. Such variation was also seen when the reference samples from film sets prepared at different times were compared [e.g., in the EB values of films plasticized with 40% sorbitol; Figs. 1(B) and 4(B)]. Whole sample sets for the stability evaluation were prepared within a short period of time to ensure similar conditions and minimize the effects of external factors on a comparison of the results.

CONCLUSIONS

OsAX plasticized with polyol can be used for the preparation of films with a variety of properties depending on the amount and type of the plasti-

cizer. Low glycerol and sorbitol contents were associated with high tensile strength, Young's modulus, and T_g and with low WVP and OP. More flexible but also more moisture-sensitive films were obtained with higher polyol contents. Results at a low polyol content (10%) indicated that glycerol might induce antiplasticization, which was detected as higher tensile strength and T_g values of the glycerol-containing films versus the films with sorbitol, whereas at a 40% plasticizer content, the difference between the glycerol- and sorbitol-plasticized films was the opposite. The use of sorbitol resulted in more effective water vapor barrier properties than the use of glycerol at both low and high plasticizer contents. At a 40% polyol content, the OP of films was also lower, and softening of films occurred at a higher RH when sorbitol was used instead of glycerol. The films were semicrystalline with similar ϕ values. Thus, the differences observed in the tensile and barrier properties of the films were not due to the differences in the crystallinity. The xylan chains in the crystallites showed a preferred orientation parallel to the surface of the film. The addition of 5% salt significantly decreased the tensile strength of the films, and this indicated the importance of the purity of the raw material. The tensile properties of glycerol-plasticized films clearly changed during 5 months of storage, whereas those of sorbitol-plasticized films were more stable. To our knowledge, this is the first report on the stability of xylan films. The film stability could be further studied (e.g., with polyol mixtures as plasticizers to reduce their migration from the film matrix). The development of films from an agrobiomass-derived byproduct, osAX, as either edible or nonedible oxygen and/or grease barriers in applications in which relatively high WVP is desired or in combination with water-resistant materials is an interesting possibility.

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