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Carboxymethylation of alkali extracted xylan for preparation of bio-based packaging films

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ABSTRACT

This study describes the synthesis of carboxymethylxylan (CMX) and investigates its suitability as a film for packaging applications. High-purity polymeric xylan was extracted from commercial bleached birch kraft pulp and converted to CMX with three different degrees of substitution (DSs). The water vapor sorption, mechanical, and barrier properties of the films prepared from CMX were tested. Increasing DS of CMX films resulted in an increase in elongation at break and a decrease in tensile strength and Young's modulus. The DS also affected the barrier properties of the films. CMX films with higher DS showed improved (reduced) oxygen permeability (OP), and the water vapor permeability (WVP) increased with DS. It was demonstrated that the carboxymethylation of xylan recovered from industrial side-streams and its conversion to packaging films could be a viable option to valorize xylan.

1. Introduction

The gradual depletion of fossil-based raw materials has promoted the development of new processing routes for the production of bio-based materials (Clark & Deswarte, 2008). In this scenario, the need for biodegradable and renewable polymers for packaging has stimulated the development of novel polymeric materials from natural sources (Hansen & Plackett, 2008).

Hemicelluloses, as the second-most abundant biopolymer on earth, represent a promising renewable raw material source for the manufacture of high-value-added products. Xylans are the most common hemicelluloses occurring in wood, mainly hardwood, as well as in annual plants such as grasses, cereals, and herbs (Ebringerová & Heinze, 2000). Xylans are particularly interesting as sustainable raw materials because they are readily available in pulp residues and side-streams of various stages of pulp production.

Birch is one of the most industrially utilized hardwood species in the northern hemisphere. Its hemicelluloses mainly consist of acetylated 4-O-methylglucuronoxylan (25–30% of dry weight of birch wood, (Koch, 2006; Sjöström, 1993)). Xylan may be isolated from certain side-streams in the pulp and textile industry or directly from appropriate plant sources and products thereof. An example of the former is the isolation from black liquor derived from kraft pulping (Lisboa, Evtuguin, Neto, & Goodfellow, 2005) or from the steeping lye generated during alkali-cellulose production (Mais & Sixta, 2004) both by membrane separation followed by precipitation in a non-solvent. An example of the latter is the alkaline extraction of hardwood chips prior to pulping (Gabrielii, Gatenholm, Glasser, Jain, & Kenne, 2000; Helmerius, von Walter, Rova, Berglund, & Hodge, 2010); extraction with dimethyl sulfoxide (Teleman, Tenkanen, Jacobs, & Dahlman, 2002) or alcohol/water (Pisarnitskii, Rubeniya & Rutitskii, 2006; Xu et al., 2006); and steam (Shimizu et al., 1998), microwave (Peng, Peng, Xu, & Sun, 2012), or hot water treatment (Testova, Chong, Tenkanen, & Sixta, 2011). Bleached hardwood kraft pulp offers an ideal raw material for the isolation of pure xylan with high yield and reasonably high molar mass. The extracted xylan does not require additional purification steps as it is free of lignin and other contaminants (Fuhrmann & Krogerus, 2009). However, it is completely deacetylated owing to the alkaline conditions applied during the cooking and bleaching processes.

Based on their macromolecular and chemical properties, xylans are considered to be a viable raw material for the manufacturing of films for packaging purposes (Hansen & Plackett, 2008; Mikkonen & Tenkanen, 2012). Xylan films are considered a potential future replacement for widely used non-degradable oxygen barrier materials, including aluminum foil and synthetic polymers such as

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ethylene vinyl alcohol and polyvinylidene chloride. When cast from aqueous solutions, some xylans can form dense, hydrogen-bonded structures with low oxygen permeability (OP). The film formation and barrier properties depend on the botanical source and chemical structure of xylans as well as on the plasticization of the films by water or added plasticizers such as polyols (Mikkonen & Tenkanen, 2012).

In preliminary investigations, it was found that pure xylan extracted from hardwood does not form films. However, the addition of plasticizers such as sorbitol, glycerol, or xylitol improves its film-forming properties (Gabrielii & Gatenholm, 1998; Grondahl, Eriksson, & Gatenholm, 2004; Zhang & Whistler, 2004). The use of chemically modified hemicellulose in composite film production has been investigated as well. Films prepared from benzylgalactoglucomannan (Hartman, Albertsson, & Sjöberg, 2006), arabinoxylan butyrate, arabinoxylan acetate (Buchanan et al., 2003), and hydroxypropyl xylan (Jain, Sjöstedt, & Glasser, 2000) exhibited major improvements in the barrier properties compared to the parent compound. Due to insufficient solubility of birch xylan in water, it was previously dissolved in sodium hydroxide to prepare films (Hansen, Blomfeldt, Hedenqvist, & Plackett, 2012). Carboxymethylation of xylan has been suggested as an alternative approach for improving its film-forming properties.

The objective of this work was to prepare carboxymethylxylan (CMX) from pulp-derived xylan and to then study the suitability of CMXs with different degrees of substitution (DSs) for films (and coatings). The films prepared from CMX with various DSs were examined for mechanical and optical properties as well as water vapor permeability (WVP) and OP. The properties of CMX films were compared with those of commercial carboxymethylcellulose (CMC) films.

2. Experimental

2.1. Materials

Bleached birch kraft pulp (BBKP) (Metsä Fiber Oy, Finland) was used as the xylan source. P_2O_5, $Mg(NO_3)_2$, and anhydrous $CaCl_2$ were purchased from Merck (Whitehouse Station, NJ, USA). D_2SO_4 (96–98% solution in D_2O, 99.5 at%D), D_2O (99.9 at%D), and CMC of 90.000 g/mol with DS 0.7 as reported by the supplier were purchased from Sigma Aldrich (St. Louis, MO, USA). Pyridine (Fluka Chemie AG, Buchs, Switzerland) and bis(trimethylsilyl)trifluoroacetamide containing 1% trimethylchlorosilane (Regisil, Morton Grove, IL, USA) were also used. Sulfuric acid (Merck, Darmstadt, Germany), sodium hydroxide (VWR, Leuven, Belgium), sodium monochloroacetate (SMCA) (Sigma–Aldrich, Steinheim, Germany), 2-propanol (VWR, Briane, France), ethanol (Altia Oyj, Rajamäki, Finland), methanol (VWR, Fontenay-sous-Bois, France), and acetic acid (Sigma–Aldrich, Steinheim, Germany) were used as reagent-grade chemicals.

2.2. Isolation of xylan

Xylan was isolated by cold caustic extraction (CCE) with 2.5 M aqueous NaOH at room temperature with a liquid-to-solid ratio of 20 L/kg for 60 min (Sixta, 2006). After the extraction, the liquor was vacuum-filtered and the pulp residue was washed until a neutral pH was obtained. The solubilized xylan was precipitated by the controlled addition of the filtrate to 4.5 M aqueous H_2SO_4. The charge of sulfuric acid was selected such that the final pH was adjusted to 2.5. After storage for up to 10–12 h, the precipitated xylan was recovered by centrifugation. In order to remove residual acid, the precipitate was washed with water in a centrifuge until the pH of the supernatant was around 5. Subsequently, the precipitate was freeze-dried and the yield was determined gravimetrically. The precipitated xylan was dialyzed in regenerated-cellulose Spectra/Por dialysis membrane tubing having a molecular weight cut-off 5000 Da to remove salts. The carbohydrate composition of the pulp samples was determined after double-stage acid hydrolysis according to NREL/TP-510-42618, and the viscosity was determined according to SCAN-CM 15:99.

2.3. Synthesis of CMX

CMX synthesis was carried out according to a previously reported method (Petzold, Schwikal, & Heinze, 2006). Briefly, 5 g of xylan (0.0378 mol of anhydroxylose units (AXUs)) was dissolved in 25% aqueous solution NaOH followed by the addition of isopropanol. The synthesis procedure was performed with increasing molar ratios of SMCA:AXU – 1:1; 2.5:1; and 4:1 – resulting in CMXs with DSs of 0.36, 0.58, and 1.13, respectively. These substances are denoted in the text as CMX 0.36, CMX 0.58, and CMX 1.13, respectively.

2.4. Analyses of non-modified xylan and CMX

Extracted xylan was hydrolyzed in one step using 4% H_2SO_4 (NREL/TP-510-42623). Subsequent analysis of the recovered neutral sugar monomers was performed by using a Dionex ICS 3000 high-performance anion exchange chromatograph with pulsed amperometric detection (HPAEC-PAD) equipped with a CarboPac PA20 column (Dionex, Sunnyvale, CA, USA). Water was used as the eluent at a flow rate of 0.4 mL/min at 30 °C.

Methylglucuronic acid (MeGlcA) was determined by the acid methanolysis/GC method (Sundberg, Sundberg, Lillandt, & Holmbom, 1996). Separation was achieved using an Agilent Technologies 6890N GC system with a flame ionization detector (FID) and an Agilent J&W column (30 m × 0.25 mm, I.D. with 0.1-μm film thickness) (Agilent Technologies, CA, USA). 4-O-MeGlcA (synthesized at BOKU, Vienna, Austria) was used as a calibration standard.

The nitrogen, carbon, hydrogen, and oxygen contents were determined using a FlashEA 1112 elemental analyzer series CHNS/O with an Autosampler MAS200R (Thermo Fisher Scientific, Bremen, Germany). To determine the sodium content, samples were dissolved/suspended in water at 0.1 mg/mL. The standard solutions (Na in H_2O (Merck)) and xylan solutions/suspensions were measured using a Jenway (ELE) PFP7 flame photometer equipped with a 589-nm filter (Bibby Scientific Limited, Staffordshire, UK). All glassware and pipette tips used in the sodium analysis were washed with nitric acid before use.

The molecular mass distribution (MMD) was examined using a size-exclusion chromatograph (SEC) equipped with an RI detector (RI-Detector ERC-7511). The column was eluted with 0.5 M NaOH at a flow rate of 1 mL/min. The SEC data were obtained using a system comprising two analytical columns (MCX 1000, 10 μm, 8 mm × 300 mm, PSS, Mainz, Germany) and a pre-column (MCX 1000, 10 μm, 8 mm × 50 mm, PSS, Mainz, Germany). The columns were calibrated with xylose (Merck, Germany); cellobiose, maltotriose, and stachyose (Fluka, Buchs, Switzerland); dextran (PSS, Mainz, Germany); and pullulan (Showa Denko, Tokyo, Japan).

Thermal analysis was carried out using a thermogravimeter TGA Q500 (TA Instruments, New Castle, DE). The samples were heated from room temperature to 700 °C at a heating rate of 10 °C/min.

^{1}H NMR spectra of xylan and CMXs after depolymerization with 25% D_2SO_4 were recorded to characterize the substitution pattern using previously reported data (Petzold et al., 2006). The spectra were measured on a 500-MHz spectrometer (Bruker Avance DPX 400) with Bruker standard pulse programs processed with Topspin software at 25 °C in a 5-mm tube.

Glycolic acid (GA) and diglycolic acid (DGA) were determined according to Alén, Niemelä, and Sjöström (1984) using an Agilent 6850 Series gas chromatograph equipped with an Agilent HP-5 column (30 m × 0.32 mm, I.D. with 0.25-μm film thickness) and an FID. The individual acid derivatives were identified by the same GC system that was equipped with a mass selective detector (GC–MSD). The interpretation of the mass spectra was based on data from previous studies (Alén & Sjöström, 1980) and performed by an HP ChemStation (A06.03) chromatography data system. For quantitative calculations, the mass-based response factors between xylitol (1.00) and GA (0.76) and DGA (0.48) were calculated according to Ackman (1964) and Verhaar and De Wilt (1969).

2.5. Preparation and characterization of films

Films were prepared from CMXs and CMC without the addition of an external plasticizer. CMXs and CMC were dissolved in deionized water at 10 g/L under magnetic stirring at room temperature for 3 h. When films were prepared for OP measurement, the CMX solutions were centrifuged and the insoluble part (CMX 0.36: 2.5 g/L; CMX 0.58: 0.3 g/L) was removed. The solutions were degassed by ultrasonication under vacuum for 5 min, cast into Teflon-coated Petri dishes, and dried at 50% RH and 23 °C. The film thickness was approximately 50 μm; however, for the OP measurement, thicker films (up to 110 μm) were prepared. The films were conditioned at 50% RH and 23 °C before analyses; however, the samples for water sorption measurements were stored in vacuum desiccators over P_2O_5 at 0% RH.

2.5.1. Water sorption

A DVS intrinsic sorption microbalance (Surface Measurement Systems, Alperton, Middlesex, UK) was used to collect water sorption isotherms of films from all CMXs. The experiments were carried out at 25 °C and RH values from 0 to 90%. The sample was hydrated stepwise in 10% RH steps by equilibrating the sample weight at each step. The moisture uptake was calculated according to Eq. (1):

$$\text{Moisture uptake} = 100\frac{W_{\text{moist}} - W_{\text{dry}}}{W_{\text{dry}}} \quad (1)$$

where W_{moist} is the sample mass equilibrated at the chosen relative humidity and W_{dry} the mass of the dry sample.

2.5.2. Tensile testing

The tensile strength, elongation at break, and Young's modulus were determined at 23 °C and 50% RH using an Instron 33R4465 universal testing machine with a load cell of 100 N; the initial grip distance was 30 mm and the rate of grip separation, 5 mm/min. A total of 12 replicate specimens (5-mm wide, ca. 70-mm long) for each film type were measured. The thickness of the specimens was measured using a micrometer (Lorentzen & Wettre, Kista Sweden).

2.5.3. Water vapor permeability

WVP was determined according to ASTM E 96/E 96M-05. The water vapor partial pressure at the underside of the film was calculated using the correction method described by Gennadios, Weller, and Gooding (1994). WVP was obtained by multiplying the water vapor transmission rate (WVTR) by the film thickness and dividing by the water vapor partial pressure difference between the two sides of the film. Three replicates of each film type were tested.

2.5.4. Oxygen permeability

The oxygen gas transmission rate (OTR) was measured using an OP tester with a coulometric sensor (Ox-Tran Twin; Modern Controls Inc., Minneapolis, MN, USA). 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 multiplying the OTR by the film thickness and dividing by the oxygen gas partial pressure difference between the two sides of the film. The specimen area was 5 cm^2. The OP measurements were performed on four replicates of each film.

2.5.5. Light transmittance

The light transmittances were scanned at wavelengths from 190 nm to 800 nm using a Shimadzu UV-2501 PC spectrophotometer (Kyoto, Japan) equipped with an integrating sphere detector. Four replicate measurements were performed. In addition, the haze of the films was determined in triplicate at a wavelength of 550 nm as described in ASTM D 1003-07.

3. Results and discussion

3.1. Isolation of xylan from BBKP by CCE

The comparison of the sugar composition of the initial (non-extracted) pulp and the final pulp (after extraction) (Table 1) showed that the anhydroglucose content increased from 75% to 92%, which was directly related to the xylan removal and reflected by the AXU content reduction from 24% to 7%. Gravimetric analysis showed that the overall mass reduction of the pulp sample after extraction was 18.3%, which could be almost exclusively attributed to the xylan removal. After purification, the final yield of isolated xylan was 14.7% (based on the original pulp). The difference in yields resulted from losses in the precipitation and washing steps of the isolation procedure.

The removal of short-chain xylan was also reflected by an increase in the pulp viscosity from 965 mL/g to 1041 mL/g. The resulting hemicellulose-lean pulp showing a relatively narrow MMD may be suitable as a dissolving pulp for the conversion to rayon fibers (Gehmayr & Sixta, 2012; Köpcke, Ibarra, Larsson, & Ek, 2010; Schild & Sixta, 2011). CCE extraction, however, can lead to the partial conversion of cellulose I to cellulose II, which is unfavorable for the production of cellulose acetate. Therefore, the nitren extraction method has been developed for the isolation of xylan, and it has been shown to have a synergistic effect on hemicellulose removal and to yield highly reactive pulps (Janzon, Saake, & Puls, 2008).

CCE was an effective method for removing xylan from BBKP, and it resulted in a final xylan concentration of 8.9 g/L (pulp consistency: 5%, initial xylose content in pulp: 24.3%). These results were in accordance with previously published data (Hamilton & Quimby, 1957). However, the xylan concentration in the extract was relatively low for further industrial processing, and it could be increased by pressure-driven membrane separation processes such as ultra- or nanofiltration. Additionally, membrane processes can efficiently remove impurities from the filtrate, including salts and other low-molecular-mass components.

The isolated and purified xylan powder was white and had high xylan purity. As shown in Table 1, xylose constitutes the main neutral sugar component (93.1%) of the recovered product, which additionally contains minor amounts of glucose (1.1%), mannose, and arabinose (less than 1%). In addition to neutral sugars, dry xylan was found to contain 2.0% of MeGlcA by acid methanolysis, reflecting a molar ratio of AXU:MeGlcA of 1:0.015 (which indicated removal of ~77% of MeGlcA) compared to a molar ratio of 1:0.067 in native xylan (Teleman et al., 2002). Strong alkaline conditions during kraft pulping and acidic conditions during bleaching result in a severe alteration of the xylan structure in birch pulp. The acetyl groups originally present in birch wood xylan are cleaved off quantitatively, which renders the xylan insoluble in water. The majority of 4-O-MeGlcA side groups linked to the xylan backbone

Table 1
Chemical composition and properties of initial birch bleached kraft pulp (BBKP), BBKP after cold caustic extraction (CCE) and isolated xylan.

	Pulp		Xylan	
	Initial	Extracted		
Intrinsic viscosity (mL/g)	965	1041	–	
Yield (% based on pulp)	(100)	81.7	14.7	
Composition	(%, o.d. basis)	(%, o.d. basis)	(% o.d. basis)	(mol%)
Glucose[a]	75.1	91.9	1.1	1.0
Xylose[a]	24.3	7.1	93.1	96.7
Mannose[a]	0.6	0.4	0.6	0.5
Arabinose[a]	n.a.[b]	n.a.[b]	0.3	0.3
4-O-MeGlcA[c]	n.a.[b]	n.a.[b]	2.0	1.5
Lignin	<0.2	<0.2	n.a.[b]	n.a.[b]
Total	100.1	99.6	97.1	100

[a] As anhydrosugars.
[b] Under detection limit.
[c] 4-O-methyl glucuronic acid.

are also lost, thus yielding a linear xylan polysaccharide that is essentially free from side-groups. A weight average molar mass (M_w) of 11,700 g/mol was determined, which corresponds to a DP_w of 89.

3.2. Characterization of alkali-extracted xylan and its carboxymethyl derivatives

In this study, the carboxymethylation of xylan was carried out after isolation and purification. However, the direct synthesis of CMX from the CCE filtrate is also possible. The DS of CMXs was determined using NMR (Fig. 1). Table 2 illustrates the total DS as well as the partial DS values at the O-2 and O-3 positions. An increase in the molar ratio SMCA:AXU leads to an increase in the DS from 0.36 to 0.58 and 1.13, respectively.

3.2.1. CMX yield and side products

During carboxymethylation, by-products such as sodium salts of GA and DGA are formed due to undesirable side reactions. It should be noted that by-products could not be completely removed from the sample even during the selected purification procedure. The purity of the obtained samples decreased with increasing DS (Table 2). This was in agreement with previously reported data (Barai, Singhal, & Kulkarni, 1997), indicating that the extent of sodium glycolate formation increases with the molar ratio of alkali and SMCA. Under these conditions, the tendency of SMCA molecules to directly react with NaOH increases. The increase in the gravimetrical yield with DS can be explained by higher sodium glycolate and sodium diglycolate contents in samples with higher DS. Therefore, the yields were recalculated to pure CMX material (Table 2). The reduction of oxygen content with increasing DS was observed; it can be related to an increased amount of side products in the sample. The sodium content for xylan and CMX 0.36 could be slightly overestimated due to possible contamination of sodium, despite careful washing of the glassware with nitric acid before analysis.

3.2.2. TGA

As shown in Fig. 2, a decrease in mass due to water evaporation was observed after the temperature was increased to ~200 °C (Liu,

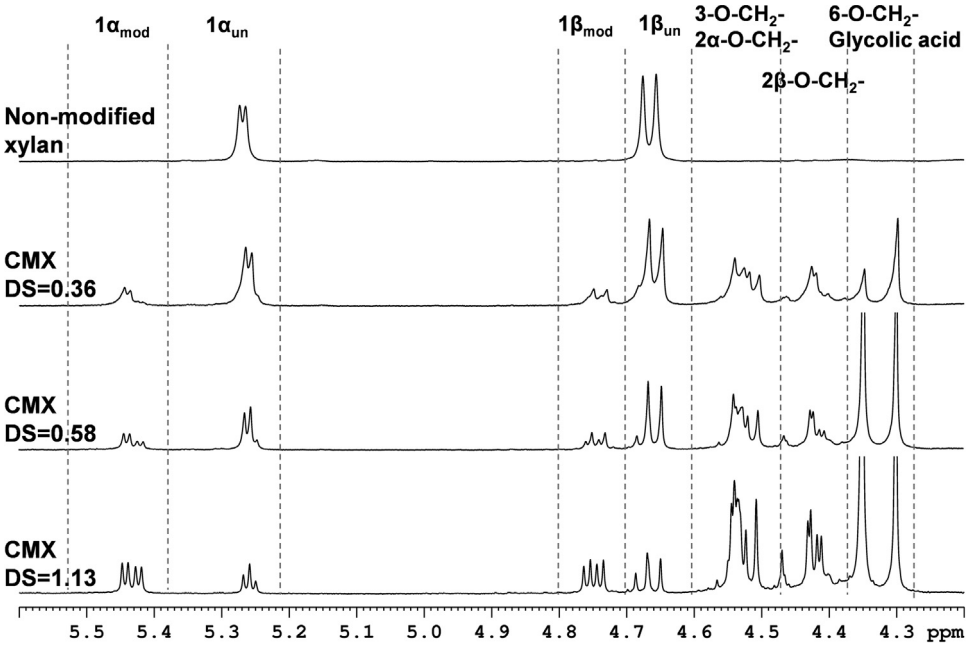

Fig. 1. ^{1}H NMR spectra (in D_2SO_4) of depolymerized non-modified xylan and CMXs with various degree of substitution (DS). Index "un" and "mod" indicate unmodified and modified in neighbored position 2, respectively.

Table 2
Degree of substitution (DS) at position O-2, O-3 and total; yield; purity and elemental composition of carboxymethyl xylans (CMXs) and non-modified xylan.

Sample name		CMX DS 0.36	CMX 0.58	CMX DS 1.13	Xylan
Molar ratio					
AXU:SMCA		1:1	1 : 2.5	1 : 4	–
DS					
O-2		0.23	0.31	0.59	–
O-3		0.12	0.26	0.53	–
Total		0.36	0.58	1.13	–
Yield					
CMX (mol %, on initial xylan)		96.7	96.6	98.8	–
Impurity (% on o.d. sample)					
GA[a]		2.2	6.9	9.4	–
DGA[a]		–	4.1	12.0	–
Total[b] (% wt. on initial xylan)		98.9	108.6	125.6	–
Empirical formula		$C_5H_{7.3}O_{4.1}Na_{0.31}$	$C_5H_7O_{4.2}Na_{0.5}$	$C_5H_{6.31}O_{4.3}Na_{0.8}$	$C_5H_8O_4$
Elemental composition[c]					
C [%]	Calc.[d]	42.3	39.7	36.3	45.3
	Found	41.6	36.7	34.3	43.2
H [%]	Calc.[d]	5.1	4.6	3.8	6.0
	Found	5.2	4.4	3.9	6.1
O [%]	Calc.[d]	47.0	46.4	45.4	48.5
	Found	46.9	44.9	42.4	50.8
Na [%]	Calc.[d]	5.5	9.3	14.5	0.0
	Found	8.1	10.3	14.8	1.3

[a] GA, glycolic acid; DGA, diglycolic acid.
[b] Gravimetrically determined.
[c] Including impurities.
[d] Theoretical calculated (including impurities).

Yu, Liu, Chen, & Li, 2008). The extent of weight loss at this phase was highest for CMX 1.13 because of its higher moisture content due to its higher hydrophilicity. The mass loss above 200 °C corresponded to the thermal decomposition of the polymer backbone and the cleavage of substituents. Xylan showed a distinct mass loss with the maximum mass loss rate in the range between 241 °C and 350 °C. At temperatures higher than 556 °C, the mass loss started to level off at a residual mass of ~20%. The thermal decomposition of CMX 0.36 and CMX 0.58 reached its highest rate at temperatures beyond 246 °C, whereas 27% and 32% of the mass resisted temperatures of 700 °C, respectively. After a first mass loss of less than 20% in the temperature range typical for xylan, CMX 1.13 experienced a further mass loss of ~25% between 271 °C and 510 °C, which could be largely related to the decomposition of GA and DGA present in the sample. At higher temperatures, the mass remained constant at ~45%.

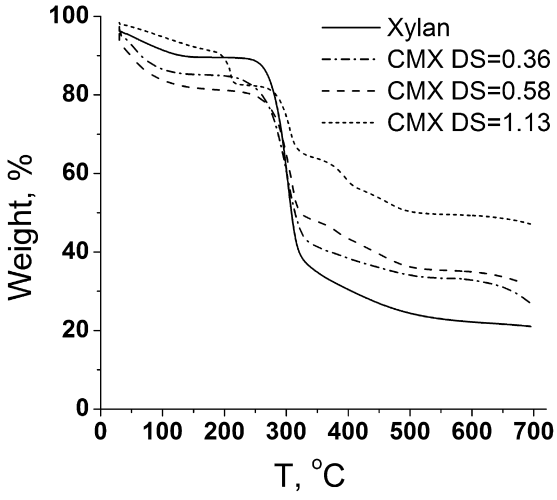

Fig. 2. Thermal gravimetric analysis (TGA) curves of non-modified xylan and carboxymethyl xylan (CMX) with degree of substitution (DS) 0.36, 0.58 and 1.13.

3.2.3. Molecular mass

The effect of the derivatization reactions on xylan's polymeric stability was monitored by SEC measurements (Table 3). Because the introduction of carboxymethyl groups may have an impact on the hydrodynamic volume of the polymer molecules and affect chain aggregation, a direct comparison of the MMD of charged and non-charged materials is not obvious. The measured M_w of xylan was in agreement with previously published data on xylan extracted from birch pulp with NaOH (Janzon et al., 2008). Considering the DSs of 0.36, 0.58, and 1.13 of the CMX samples, DP values of 106, 92, and 81 were respectively determined. The DP was calculated according to Eq. (2):

$$DP = \frac{M_w\,(SEC)}{132 + DS \times M_{CH_2COONa} - DS \times M_H} \quad (2)$$

where DP is degree of polymerization, M_w is weight average molar mass determined by SEC, 132 is molar mass of anhydroxylose unit (g/mol), M_{CH_2COONa} is molar mass of CH_2COONa, M_H is molar mass of hydrogen.

These results suggest that only minor chain degradation occurred during the derivatization of xylan. Further, the slightly lower polydispersity of the CMX samples (1.62–1.69) compared to that of xylan (1.79) indicated a more uniform MMD.

Table 3
Number average molecular mass (M_n), weight average molecular mass (M_w), polydispersity (M_w/M_n) and degree of polymerization (DP) of xylan and carboxymethyl xylans (CMXs) determined by SEC.

Sample name	M_n	M_w	M_w/M_n	DP
Xylan	6500	11,700	1.79	89
CMX 0.36	10,100	17,100	1.69	106
CMX 0.58	10,150	16,450	1.62	92
CMX 1.13	10,900	18,100	1.66	81

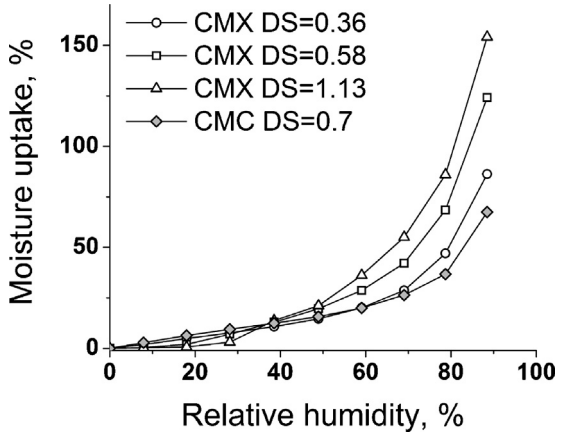

Fig. 3. The water sorption isotherms of films prepared from carboxymethyl xylan (CMX) with degree of substitution (DS) 0.36, 0.58, 1.13. Results for carboxymethyl cellulose (CMC) are included for comparison. The results are averages of two measurements.

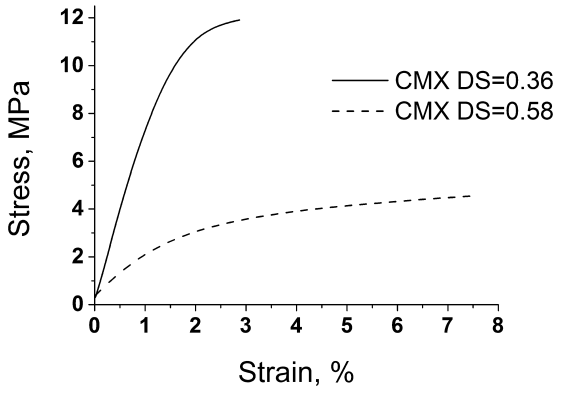

Fig. 4. Stress–strain curves of carboxymethyl xylan (CMX) films obtained using an Instron tensile tester at 50% RH. The results are averages of 12 replicate measurements.

3.3. Properties of CMX films

Preliminary experiments showed that alkali-extracted birch xylan did not form self-supporting continuous films from a water suspension but resulted in small, fragmented film pieces. The poor film-forming ability of xylan was most likely due to its low solubility in water. Therefore, our approach involved the carboxymethylation of xylan to obtain water-soluble derivatives. All three studied CMXs formed cohesive and flexible films without the addition of external plasticizer.

3.3.1. Water vapor sorption

The moisture sorption properties of CMX films were determined and compared with those of CMC films. All films showed increased moisture uptake with increasing RH, as expected (Fig. 3). At low RH, the CMX films showed lower moisture uptake compared to the film from the CMC. In contrast, at higher RH, the trend was opposite, and the higher moisture uptake for the CMX films (all DS) was observed. The exocyclic CH_2—OH groups of cellulose, significantly higher molar mass, and residual uronic acids in CMX could play a role in the lower moisture uptake of CMC films at high RH compared to films from CMX 0.58, whose DS was close to that of the CMC used. In comparison to previously studied films from rye endosperm arabinoxylan (Mikkonen, Heikkilä, Willför, & Tenkanen, 2012), which is naturally water soluble due to the high content of arabinofuranosyl branches, the moisture uptake of films from CMXs and the studied CMC was clearly higher at high RH, indicating the hydrophilic nature of the carboxymethyl groups.

At RH below 40%, the moisture uptake of CMX films increased with decreasing DS. In contrast, at higher RH, from 50% to 90%, the effect was the opposite. This phenomenon was similar to that observed previously for films from other polysaccharides such as wheat starch (Godbillot, Dole, Joly, Rogé, & Mathlouthi, 2006) and spruce galactoglucomannan (Mikkonen, Heikkilä, et al., 2012; Mikkonen et al., 2011) containing different amounts of added polyol (glycerol or sorbitol) as plasticizer. In these studies, increasing plasticization of films decreased their moisture uptake at low RH and increased it at high RH. The finding was explained by polyols occupying the water sorption sites of films at low RH and increasing the moisture uptake of films at high RH because of their hydrophilicity and strong capacity to bind water. In the present study, the water-binding behavior of carboxymethyl groups in the CMXs showed similar trends to those of external polyol plasticizers. However, the function of acidic carboxymethyl groups, unlike that of neutral polyols, is dependent on the pH of the system. The pH of the aqueous CMX solutions was clearly above the pK_a of carboxyl group; thus the CMXs were in ionic form. This could affect the molecular arrangement of the CMX molecules due to ionic repulsion, as well as increase the hydrophilicity of the materials. The lower moisture uptake of films from low DS CMXs at high RH could also be related to the presence of higher amounts of unsubstituted regions in the xylan chain, which could increase interchain aggregation via hydrogen bonds, thus preventing parts of the CMX from absorbing moisture.

Water acts as a plasticizer of polysaccharides and affects the functional properties of films (Talja, Helén, Roos, & Jouppila, 2007). To obtain comparable results, the mechanical and permeability analyses of films are usually conducted at a controlled RH of ~50%, which was also the case in the present study. The moisture uptake of CMX films at 50% RH increased with increasing DS and was 14.6%, 19.6%, and 21.2% for CMX 0.36, CMX 0.58, and CMX 1.13 films, respectively. At higher RH (90%), CMX 0.36 films absorbed ~90% water, whereas the moisture uptake of CMX 0.58 and CMX 1.13 films was clearly higher, being 125% and 155%, respectively. Further testing of CMX 1.13 films was not performed owing to their softness at 50% RH.

3.3.2. Mechanical properties

The mechanical properties of packaging films determine their suitability for applications that require resistance to mechanical stress during use. As coatings, the coated object provides support for the film, reducing the requirement for its mechanical strength. The DS of CMXs clearly affected the tensile characteristics of the films (Fig. 4). The tensile strength and Young's modulus of CMX 0.36 films were higher and the elongation at break lower than those of CMX 0.58 films (Table 4). This could be due to the function of

Table 4
Mechanical and optical properties of carboxymethyl xylan (CMX) films (mean ± standard deviations from 12 measurements for tensile testing or three to four measurements (water vapor permeability (WVP), oxygen permeability (OP), light transmittance, and haze).

Property	CMX 0.36	CMX 0.58	CMC 0.7
Young's modulus (MPa)	800 ± 280	200 ± 40	3800 ± 280
Elongation at break (%)	3 ± 1	8 ± 2	4 ± 1
Tensile strength (MPa)	12 ± 5	5 ± 1	58 ± 7
OP (cm^3 μm/(m^2 d kPa))	23 ± 13	6 ± 1	7 ± 4
WVP (g mm/(m^2 d kPa))	19 ± 2	38 ± 2	19 ± 2
Light transmittance, 550 nm (%)	92 ± 1	91 ± 0.1	92 ± 0.2
Haze, 550 nm (%)	12 ± 4	6 ± 0.1	2 ± 1

carboxymethyl groups as internal plasticizers and/or higher water content and the plasticizing effect of water on CMX 0.58 films at 50% RH. A higher number of carboxymethyl groups attached to CMX could decrease the intermolecular forces between the polymer chains, resulting in a lower tensile strength of films. These results differ from those reported by Rachtanapun, Luangkamin, Tanprasert, and Suriyatem (2012), who suggested that an increasing DS of durian rind CMC increased the tensile strength of films. In addition, the presence of sodium glycolate and sodium diglycolate, which are formed as side products, weakens the mechanical performance of the CMX films. This was also reported for oat spelt arabinoxylan films, where the tensile strength decreased at a salt concentration of only 5% (Mikkonen et al., 2009). The decreasing tensile strength of CMX with increasing DS parallels the increasing amounts of side products (Table 4).

It appeared that the optimal range of the degree of carboxymethyl substitution of alkali-extracted birch xylan is between 0.36 and 0.58; it enables film formation from water solution and yields films with sufficient mechanical properties for easy handling. However, further study would be required to identify the optimal DS more precisely. The M_w significantly affects the mechanical strength properties, as demonstrated by films prepared from CMC with a molar mass of 90,000 g/mol (Table 4). Previously studied films from high-molar-mass rye endosperm arabinoxylan (184,000 g/mol) were also stronger and stiffer (tensile strength 64 MPa and Young's modulus 1.8 GPa) than the CMX films and had rather similar elongation at break to that of CMX 0.58 films (Mikkonen, Pitkänen, et al., 2012). However, films prepared from birch and cotton stalk xylan with the addition of lignin had significantly lower tensile strength (Goksu, Karamanlioglu, Bakir, Yilmaz, & Yilmazer, 2007). The present tensile testing results of CMX films were similar to those obtained previously for films from polyol-plasticized oat spelt arabinoxylan (Mikkonen et al., 2009), which had a molar mass of 32,000 g/mol. The improvement of the mechanical properties of CMX-based films might require their blending with other, larger polymers.

3.3.3. Barrier properties

The WVP is directly related to the hydrophilic nature of the film. The WVP of CMX 0.58 films was higher than that of CMX 0.36 films owing to an increase in hydrophilicity with increasing DS. Similarly, the increase in the WVP of films with increasing DS of *Mimosa pigra* CMC was reported by Rachtanapun and Rattanapanone (2011). Therefore, CMX 0.36 films were better water vapor barriers than CMX 0.58 films, with a WVP similar to that of CMC films. However, all the studied films had much higher WVP than previously studied films, for example, oat spelt arabinoxylan films (Mikkonen et al., 2009) or rye bran arabinoxylan films (Sárossy, Tenkanen, Pitkänen, Bjerre, & Plackett, 2012). In general, the water sensitivity of polysaccharide-based films is one of the reasons for their limited use as packaging materials. This property, however, could be exploited in water-soluble edible films, or it could be overcome by developing laminate films consisting of a water-sensitive inner layer protected with hydrophobic outer layers.

Polysaccharides are generally good oxygen barriers at low to moderate RH owing to the dense packing of polymers by hydrogen bonding. This was also the case with the CMX films; in particular, CMX 0.58 films showed promising oxygen barrier properties with an OP comparable to that of CMC films (Table 4). This is most likely a result of better film formation of CMX 0.58 due to its enhanced water solubility and thus more densely organized structure compared to that of the CMX 0.36 films. However, the obtained OP values were not as low as those recently reported for spruce arabinoglucuronoxylan (Escalante et al., 2012) and rye bran arabinoxylan films (Sárossy et al., 2012). The OP results indicate that CMX films could be suitable for packaging or coating of fresh fruits or vegetables that require a certain amount of oxygen for respiration. A drawback of xylan films is that their OP may greatly increase at high RH (Mikkonen & Tenkanen, 2012). Due to the hygroscopic character of the CMX films, their applications may require development of multilayer structures with a moisture barrier component.

The light transmittance and haze of CMX films were determined and compared with those of CMC films (Table 4). Both CMX films were highly transparent with a light transmittance of ~90% at visible regions of the spectra (550-nm wavelength). There was more variation in the haze of the films, which was ~12% for CMX 0.36 films and only 6% for CMX 0.58 films. Thus, the CMX films showed slightly increased light transmittance and decreased haze with decreasing DS. These results supported the previously discussed observation that increasing the DS of CMXs increases the water solubility and homogeneity of the materials.

Both studied CMX films blocked the transmission of light in the UV region of the spectrum. The high transparency and low haze of CMX films, which are similar to those of CMC films (Table 4), indicated that these films could be visually appealing as packaging materials and that products packaged in such films could be seen clearly through the packaging.

4. Conclusions

High-purity xylan with M_w of 11.5 kg/mole was isolated from lignin-free birch paper-grade kraft pulp. The process allows the extraction of up to 60% of xylan present in the pulp (14.7% on o.d. pulp). Unlike the native form, the recovered xylan product approximates a linear polysaccharide, is essentially free from acetyl side chains, and has a very low amount of 4-O-MeGlcA substituents, with an average molar ratio of 1:65 AXU. The purified xylan was carboxymethylated to DS levels of 0.36, 0.58, and 1.13, respectively. Self-supporting continuous films could not be formed from pure birch xylan. However, carboxymethylation of xylan was shown to be a viable pathway for producing flexible and highly transparent films. With increasing DS, the thermal stability and the moisture uptake of CMX films at 50% RH increased. The testing of homogeneous CMX 1.13 films was not possible owing to their high hydrophilicity and resulting softness. Among the two remaining CMX films, the one with the higher DS (CMX 0.58) showed a higher elongation at break, whereas the CMX 0.36 film had clearly superior tensile strength and elastic modulus, presumably due to the lower side product content. CMX 0.36 showed lower WVP, which could be related to its lower hydrophilicity. Furthermore, CMX 0.58 films showed lower OP than CMX 0.36 films owing to their better water solubility and the resulting more densely organized structure.

Overall, this study demonstrated that carboxymethylation can potentially be used to upgrade birch pulp xylan to bio-based and biodegradable film-forming materials without the addition of external plasticizers; these films have suitable oxygen barrier properties for, for example, packaging or coatings for fruits and vegetables.

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