Carbohydrate Polymers 250 (2020) 116916

Contents lists available at ScienceDirect

Carbohydrate Polymers

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

Bio-based films from wheat bran feruloylated arabinoxylan: Effect of extraction technique, acetylation and feruloylation

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ARTICLE INFO

Keywords:
Arabinoxylan
Wheat bran
Subcritical water extraction
Ferulic acid
Acetylation
Barrier properties
Antioxidant activity

ABSTRACT

This study demonstrates the potential of feruloylated arabinoxylan (AX) from wheat bran for the preparation of bioactive barrier films with antioxidant properties. We have comprehensively evaluated the influence of the structural features and chemical acetylation of feruloylated AX extracted by subcritical water on their film properties, in comparison with alkaline extracted AX and a reference wheat endosperm AX. The degree of substitution (DS) of AX had a large influence on film formation, higher DS yielded better thermal and mechanical properties. The barrier properties of AX films were significantly enhanced by external plasticization by sorbitol. Chemical acetylation significantly improved the thermal stability but not the mechanical or barrier properties of the films. The presence of bound ferulic acid in feruloylated AX films resulted in higher antioxidant activity compared to external addition of free ferulic acid, which demonstrates their potential use in active packaging applications for the preservation of oxygen-sensitive foodstuff.

1. Introduction

Over the past few decades, large research efforts have been made to exploit by-products from agricultural crops for the development of novel bio-based materials. Wheat bran represents an illustrative example of such by-products as it is generated in large volumes. The worldwide production of wheat reached 735 M ton in 2018 (FAOSTAT, 2018), generating thereby up to 110 M tons of wheat bran considering that bran represents 15 % of the wheat kernel (Corke, 2004). A major part of wheat bran is composed of polysaccharides (53–60 %), followed by proteins (14–20 %), lignin (9 %), phenolic acids (0.2−0.3 %), and fat and other components (10.9 %) (Apprich et al., 2014; Ruthes, Martínez-Abad, Tan, Bulone, & Vilaplana, 2017). The main polysaccharide constituent of wheat bran is arabinoxylan (AX) accounting for 20–40 % of its total composition. Wheat bran AXs can be decorated by phenolic acids, essentially by ferulic acid (FA) at the arabinose residues (Kim, Tsao, Yang, & Cui, 2006; Ruthes et al., 2017). This feruloylation confers functional and bioactive properties to wheat bran AXs, such as antioxidant potency. Wheat bran AXs are typically extracted by acidic or alkaline solvents, which can disrupt the covalent and non-covalent bonds between the cell wall components and enable obtaining AXs with high yields (Zhang, Smith, & Li, 2014). Alternatively, a high portion of AXs can be extracted from the cell wall using subcritical water extraction (SWE), which maintains the polymeric structure of the AXs and more importantly, preserves their functional phenolic acids, unlike alkaline extraction (Ruthes et al., 2017).

Cereal AXs represent a valuable renewable matrix for the design of bio-based materials, due to their polymeric structure and favorable intrinsic properties (i.e. high molar mass, reactive hydroxyl groups and feruloylation). The relatively high molar mass of cereal AXs is

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https://doi.org/10.1016/j.carbpol.2020.116916
Received 19 April 2020; Received in revised form 4 August 2020; Accepted 5 August 2020
Available online 15 August 2020

fundamental for the preparation of self-standing films with good mechanical properties. The hydrogen bonding between adjacent AX chains creates a dense macromolecular network that leads to low mobility and hence, excellent barrier properties to oxygen in film applications, similar to other polysaccharide-based films (Heikkinen et al., 2013). Furthermore, the natural variability of AXs brought by their reactive hydroxyl groups enables versatile modification strategies towards improving their material properties. Hereof, acetylation has been acknowledged as a modification tool to improve the properties of AX-based films replacing the hydroxyl groups by acetyl, thus increasing water resistance and improving thermal stability (Ayoub, Venditti, Pawlak, Sadeghifar, & Salam, 2013; Egues et al., 2014; Morais de Carvalho, Berglund et al., 2019; Morais de Carvalho, Marchand et al., 2019). However, the comparative acetylation of wheat bran AXs extracted by different techniques and their subsequent application into film materials has not been assessed.

In this work, we evaluate the potential of feruloylated arabinoxylans extracted from wheat bran by subcritical water for the development of bioactive barrier films with antioxidant properties. To the best of our knowledge, this is the first study on the film forming properties of wheat bran AX with covalent ester-bound ferulic acid. We have comprehensively investigated the influence of extraction procedure, chemical acetylation and feruloylation on the film-forming performance of native and acetylated AXs, and the molecular factors that influence their material, barrier and scavenging properties. For this, we isolated AXs from wheat bran using SWE and alkaline extraction to prepare films with and without plasticization, in comparison with a reference wheat endosperm AX. We performed chemical modification of the wheat bran AXs by acetylation to assess the potential internal plasticization and to modulate their hydrophobicity when preparing films. Finally, the influence of external incorporation of free FA compared to bound FA in feruloylated AX was evaluated. The radical scavenging, morphological, mechanical, barrier and thermal properties of the native and acetylated AX films developed from the native AX were analyzed to evaluate their performance in potential food packaging applications.

2. Material and methods

2.1. Materials

Wheat bran was kindly provided by Lantmännen (Stockholm, Sweden), which was composed of 27.9 ± 0.7 % AX, 14 ± 0.0 % protein, 13 ± 0.3 % starch and 0.3 ± 0.0 % FA. All chemicals and enzymes were purchased from Sigma-Aldrich (Stockholm, Sweden). Low viscosity wheat endosperm arabinoxylan (WAX) and the total starch assay kit were purchased from Megazyme (Wicklow, Ireland).

2.2. Extraction and modification of the AX fractions

2.2.1. Extraction of arabinoxylans

Wheat bran (WB) was pretreated by α-amylase before the extraction to remove the starch. Briefly, WB was solubilized in 50 mM sodium phosphate buffer (pH 7.0) at a ratio of 1:10 (w/v) and heated to 90 °C for 8 min to gelatinize starch. The slurry was cooled down to 37 °C and treated with α-amylase (16 U mg^{-1}) for 5 h under constant stirring. A second dose of α-amylase was then added to the mixture and mixed for further 17 h. Destarched wheat bran (DWB) was washed with cold absolute ethanol twice with centrifugation in between (11,325 *g*, 30 min, 4 °C) and dried in an oven at 65 °C. The starch content was determined using the Megazyme Total Starch Assay Kit to verify the starch removal.

The subcritical water extraction (SWE) of arabinoxylans from DWB was carried out using a pilot scale rotary autoclave at 160 °C, as described in Rudjito, Ruthes, Jiménez-Quero, and Vilaplana (2019). In brief, DWB was mixed with tap water at a ratio of 1:10 (w/v) and the extraction was performed for 30 min, followed by the filtration of the extract. Filtered samples were then precipitated with 95 % ethanol at a ratio of 1:4 (v/v) at 4 °C for 24 h, recovered by centrifugation (11,325 *g*, 15 min, 4 °C) and washed with 75 % ethanol. Recovered samples were resuspended in distilled water and then freeze-dried. The freeze-dried subcritical water extracts were named as FAX (feruloylated arabinoxylan).

The alkaline extraction was performed according to the method described by Ruthes et al. (2017). Briefly, DWB was mixed with 0.5 M sodium hydroxide (NaOH) at a ratio of 1:8 (w/v) at 80 °C for 16 h under constant stirring. The extract was recovered by centrifugation (11,325 *g*, 30 min, and 4 °C) and dialyzed for 72 h using a 20 kDa MWCO dialysis membrane (Spectrumlabs, Breda, The Netherlands). The extract was then freeze-dried and named as NAX (non-feruloylated alkaline arabinoxylan).

2.2.2. Acetylation of arabinoxylans

The acetylation of FAX and NAX, and the commercial wheat endosperm arabinoxylan (WAX) was performed based on the per-*O*-acylation method (Morais de Carvalho, Berglund et al., 2019; Zhang, Zhang, Liu, & Ren, 2016). Briefly, AXs were mixed with dimethyl sulfoxide (DMSO) and N-methylimidazole (NMI) at a ratio of 22:2:1 (mg AX:mL DMSO:mL NMI) at 100 °C for 5 h and at room temperature (21−23 °C) for 19 h. Acetic anhydride (21.8 mL) was then added dropwise to the mixture and stirred for 24 h at room temperature. The precipitation and recovery of reaction products were performed as described by Morais de Carvalho, Marchand et al. (2019). A second acetylation under the same conditions was implemented on the freeze-dried samples to maximize the degree of acetylation. The acetylated products of FAX, NAX and WAX were named as AcFAX, AcNAX and AcWAX, respectively.

2.3. Compositional and structural analysis of the AX fractions

2.3.1. Monosaccharide analysis

The monosaccharide composition of the wheat bran extracts and the acetylated samples was determined after two-step methanolysis (Martínez-Abad, Giummarella, Lawoko, and Vilaplana (2018). The monosaccharide analysis was performed using high-performance anion exchange chromatography with pulsed amperometric detection (HPAEC-PAD) system (Dionex ICS 3000, Sunnyvale, CA, USA) equipped with a CarboPac PA1 column. The eluent program was the same as in McKee et al. (2016). The quantification of the monosaccharides was performed by calibration with neutral sugars and uronic acid standards at concentrations between 0.005 and 0.1 g/L. The measurements were done in triplicates.

2.3.2. Phenolic acid profiling

The phenolic acid content of all samples (duplicates) was determined after saponification using 2 M NaOH (20:1, w/v) at 30 °C overnight, subsequent acidification by 37 % HCl and extraction with ethyl acetate. The extracted samples were resuspended in methanol and analyzed by a Waters HPLC system (Waters 2695 separation module, Waters 2996 photodiode array detector; USA) coupled to a UV/Vis detector, equipped with a C18 guard column and an SB-C18 separation column (Zorbax SB-C18 5 μm particle size, 4.6 × 250 mm, Agilent, Santa Clara, CA, USA) at 1 mL/min using a gradient of 2% acetic acid and methanol, as described in Menzel, Gonzalez-Martinez, Chiralt, and Vilaplana (2019). A standard calibration was recorded at 270 nm and 325 nm using caffeic acid, p-coumaric acid, FA, cinnamic acid and dimer of FA (5-5ACFE) at concentrations between 0.005 g/L and 0.1 g/L.

2.3.3. Molecular weight distribution

The apparent molecular weight distributions of all the samples were determined by size exclusion chromatography (SECcurity 1260, Polymer Standard Services, Mainz, Germany) coupled to a refractive index detector using standard calibration by pullulan as described by Ruthes et al. (2017). The samples were dissolved in the SEC eluent consisting of DMSO supplemented with 0.5 % w/w lithium bromide (LiBr) at a

concentration of 3 mg/mL.

2.3.4. Fourier transform infrared spectrometry (FTIR)

FTIR spectra were recorded using a Perkin Elmer Spectrum 100 FTIR instrument (Norwalk, CT) equipped with a single reflection accessory unit (Golden Gate, Graseby Speac Ltd, Kent, England) for Attenuated Total Reflection (ATR). 16 scans were recorded for each sample in the spectral range of 600−4000 cm^{-1} at a resolution of 4 cm^{-1}. Automatic baseline correction was done using Spectrum software from Perkin Elmer.

2.3.5. Degree of acetylation

The degree of acetylation (DA) was determined after saponification with 0.8 M NaOH at 60 °C, neutralization with 37 % hydrochloric acid and following filtration (0.2 μm syringe filter, nylon, Thermofisher, USA) according to Bi, Berglund, Vilaplana, McKee, and Henriksson (2016). The released acetic acid was analyzed in an Ultimate-3000 HPLC system (Dionex, Sunnyvale, CA, USA) equipped with a UV/Vis detector (210 nm, Dionex, Sunnyvale, CA, USA) and a Phenomenex Rezex ROA-Organic acid column (300 × 7.8 mm; Phenomenex, Torrance, CA, USA) using a mobile phase of 2.5 mM sulfuric acid. Acetic acid quantification was performed by calibration (1, 3, 6, 10, 30, 60 mM acetic acid) and propionic acid as internal standard (6.25 mM). The DA was calculated according to Morais de Carvalho, Berglund et al. (2019). DA was corrected based on the purity of AX in all samples in order to eliminate the impact of possible acetylation of hexose fractions.

2.4. Film preparation and characterization of material properties

2.4.1. Solvent casting of AX films

Non-plasticized films were prepared from FAX, NAX, and WAX by resuspending the dry samples in distilled water (10 g/L) and mixed for 3 h at 50 °C. The AXs solutions were degassed by ultrasonication for 5 min, casted on Teflon plates and dried at 30 °C. For *sorbitol plasticized films* of FAX, NAX, and WAX, 30 % (w/w of AX) sorbitol was added to the suspensions after 2 h of mixing and the preparation of the films was continued as described above. Plasticized films were named as FAXSor, NAXSor, and WAXSor, respectively.

To compare the effect of bound and free FA on the film properties, FA was mixed with WAX at a concentration of 8 mg FA/g AX (corresponding to the content of covalently-bound FA in FAX) and films were casted as described above. Sorbitol was added to the plasticized film at 30 % (w/w). These films were named as WAX+FA and WAXSor+FA, respectively.

The films of AcFAX, AcNAX, and AcWAX were casted from acetylacetone using the same AX concentration (10 g/L). The suspensions were mixed overnight at room temperature and then ultrasonicated for 5 min. Triacetin was used as a nonpolar plasticizer at 30 % v/w AX for the *plasticized films*. *Plasticized* and *non-plasticized* film solutions were casted on Teflon plates followed by drying at room temperature. Only plasticized samples of the acetylated AX formed continuous films and these films were further named as AcFAX, AcNAX and AcWAX, respectively. The formulation of the different prepared films was presented in Supplementary Table S1.

2.4.2. Field emission scanning electron microscopy (FE-SEM)

The cross-sectional images of the films were obtained using a Hitachi TM-1000 FE-SEM instrument (Tokyo, Japan) at an acceleration voltage of 1.0–5.0 kV. Prior to imaging, all the film samples were Pt/Pd sputtered for 15 s using Cressington sputter coater, 208HR (Watford, UK) under vacuum.

2.4.3. Tensile testing

Mechanical properties of the films were determined using a universal testing machine (Instron 5944, Norwood, MA, USA) fitted with a 500 N load cell. The conditioned films (23 °C, 50 % RH, 3–7 days) were cut into specimens with average width of 5 mm. The initial distance between the grips of the testing machine was 10 mm and the stretching rate was 10 mm/min. The stress-strain curve was recorded for 5 specimens for each film sample. The width and thickness of the specimens were measured at 3 different points.

2.4.4. Thermal analysis

Thermal properties of the films were characterized using differential scanning calorimetry (DSC 1, Mettler Toledo Inc., Greifensee, Switzerland) and thermogravimetric analyzer (TGA/DSC 1 Mettler-Toledo, Columbus, OH, USA) in duplicates. The glass transition temperature (T_g) of the films was determined from the DSC curves under a nitrogen flow of 50 mL/min at a heating rate of 10 °C/min. Approximately 4 mg of film samples were analyzed according to the following temperature program: heating from 25 °C to 125 °C, holding for 5 min at 125 °C, cooling from 125 °C to -25 °C, holding for 5 min at -25 °C, and heating from -25 °C to 450 °C. T_g was determined from the 2nd heating cycle.

Thermogravimetric analysis (TGA) was performed by heating approximately 4 mg of film samples from 25 °C to 750 °C at a heating rate of 10 °C/min under a nitrogen flow of 50 mL/min. The thermogravimetric (TG) and the first derivative thermogravimetric (DTG) curves were generated using the Mettler-Toledo STAR^e Evaluation Software.

2.4.5. Oxygen permeability

The oxygen gas transmission rate (OTR) of the films was measured using Ox-Tran equipment (MOCON Model 2/20, Minneapolis, MN, USA). The films were conditioned at 50 % RH for 24 h prior to testing and then placed into the equipment using aluminum masks with an O_2-exposure area of 5 cm^2. The measurements were performed at 25 °C and 50 % RH in duplicates. The oxygen permeability (OP) was calculated by multiplying the OTR by the average thickness of the films determined at 5 different points.

2.4.6. Water vapor permeability

The water vapor permeability (WVP) was determined according to the ASTM E 96/E 96 M − 05 standard (ASTM, 2016). Pre-conditioned film samples were sealed onto permeability cups (VF2200, TQC Sheen, Molenbaan, The Netherlands) containing 8.5 g dry calcium chloride ($CaCl_2$) (0 % RH), exposing 10 cm^2 of the film to water vapor and leaving 6 mm air gap between the desiccant and the underside of the sample. The cups were then placed into pre-equilibrated cabinets containing oversaturated solutions of magnesium nitrate (53 % RH) at 21 °C. The cups were weighed periodically for 24 h (1.5 h–24 h) and the RH was measured in the cabinets prior to each weighing using an RH-meter. The weight loss *versus* time was plotted and the water vapor transmission rate (WVTR) and WVP were calculated and corrected according to Gennadios, Weller, and Gooding (1994). The measurements were performed in duplicates.

2.4.7. Radical scavenging activity

The radical scavenging activity of the AXs and the films was determined by the 1,1-diphenyl-2-picrylhydrazyl ($DPPH^•$) assay according to Brand-Williams, Cuvelier, and Berset (1995) with minor modifications. In brief, 100 μM methanolic $DPPH^•$ solution was mixed with different amounts of aqueous sample solutions (1, 6, 10, 20, 40, 60, 80, 100 μL) and the reaction mixtures were kept in the dark at room temperature for 30 min. The resulting absorbances were measured at 517 nm using a microplate reader (Clariostar Plus, BMG LABTECH, Ortenberg, Germany). The decrease in the absorbance of $DPPH^•$ after 30 min was measured and the radical scavenging activity was expressed as half-maximal effective concentration (EC_{50}) (mg sample/mg $DPPH^•$), which corresponds to the concentration of sample required to decrease the initial concentration of $DPPH^•$ by 50 %. The methanolic solution of FA (500 μg/mL) and the aqueous solution of ascorbic acid (50 μg/mL) were used as positive controls and methanol was used as blank.

2.5. Statistical analysis

Statistical analysis was performed by the IBM SPSS Statistics 26 software for the comparison of the acetyl content and DA of the extracts, and the mechanical properties of film samples using Tukey's HSD post hoc test. The comparison of thermal, barrier and radical scavenging activity of films was done by a simple *t*-test. Statistical significance was set at $p < 0.05$ level.

3. Results and discussion

3.1. Composition and molecular structure of the wheat bran arabinoxylan fractions

The choice of extraction method influences the composition and structure of the extracted AXs, which in turn affects the properties of materials developed from them (Ruthes et al., 2017). Therefore, we initially evaluated the carbohydrate, phenolic acid composition and radical scavenging activity of the AX fractions isolated by subcritical water (FAX) and alkaline extraction (NAX) and compared to a commercially available AX from wheat endosperm (WAX) as a reference material (Table 1). The extraction yield of the SWE was 7.5 % whereas the yield of the alkaline extraction was 31.1 %. This difference can be explained by the harsh conditions of the alkaline extraction that proceeds by breaking the covalent and non-covalent bonds between AX-AX and AX-other cell wall polymers (i.e. proteins, phenolic acids, lignin and cellulose). The sugar analysis demonstrated the high purity of the AX fractions extracted from wheat bran using SWE (FAX) and alkaline extraction (NAX), with AX contents between 80–90 % of the total carbohydrate content (dry basis). Significantly lower Ara/Xyl ratio of FAX (0.2) compared to NAX (0.7) was attributed to the susceptibility of the Ara moieties to hydrolysis at high temperatures during SWE (Reisinger et al., 2013; Sternemalm, Hoije, & Gatenholm, 2008). Another reason for this difference may be that alkali is capable of extracting highly substituted AX from the outer layers of wheat bran whereas SWE releases polysaccharides from aleurone and intermediate layers where AXs are less substituted (Barron, Surget, & Rouau, 2007; Ruthes et al., 2017, 2020). The AX content and the Ara/Xyl ratio of the commercial WAX were 99.2 % and 0.6, respectively. FAX, NAX and WAX showed large differences in the glucose content, which are related to the differences in their origin and extraction processes. Alkaline extraction results in the cleavage of ester bonds between cell wall polymers, thus releasing larger amounts of arabinoxylan from wheat bran as shown by Ruthes et al. (2017). On the other hand, starch and mixed-linkage β-glucan show preferred extractability from cereal brans under subcritical water conditions, which therefore explains their higher content in FAX (Rudjito, Ruthes, Jiménez-Quero, & Vilaplana, 2019; Ruthes et al., 2020). FA was determined as the predominant phenolic acid in FAX (79.0 %), whereas no phenolic acids were detected in NAX and WAX, confirming the preservation of FA by SWE. The antioxidant potency of FAX, NAX and WAX was determined using the DPPH$^{\bullet}$ assay and the EC_{50} value of FAX was measured as 17.7 mg/mg DPPH$^{\bullet}$ whereas it was 53.2 mg/mg DPPH$^{\bullet}$ for NAX, probably due to the presence of minor lignin components released by alkaline treatment (Maes & Delcour, 2001). Besides, WAX did not show any DPPH$^{\bullet}$ scavenging activity. As expected, the higher activity of FAX was related to its high FA content introducing a very strong radical scavenging activity, as implied by the activity of the FA standard used in the assay.

The molar mass distributions of the AX fractions were determined by size exclusion chromatography (Fig. 1a). FAX and WAX showed monomodal molar mass distributions centered at 8×10^4 and 1-2 $\times 10^5$ g mol^{-1}, respectively. On the other hand, a bimodal distribution was observed in NAX with a low molar mass population (2×10^3 g mol^{-1}) and a high molar mass population (1×10^5 g mol^{-1}). The low molar mass population in NAX corresponded to the presence of a minor population of oligosaccharide fractions that was not efficiently removed during the dialysis process (Ruthes et al., 2017).

Table 1
Extraction yields, chemical composition, average molar mass, degree of acetylation and radical scavenging activity of the native and acetylated arabinoxylans.

	FAX	NAX	WAX	AcFAX	AcNAX	AcWAX
Extraction yield (%)[a]	7.5	31.1	n.a	n.a.	n.a.	n.a.
Carbohydrate content (mg/g DW)[b]	944.2 ± 51.3	822.1 ± 34.8	992.1 ± 95.6	465.5 ± 64.6	385.2 ± 6.1	415.0 ± 15.1
Ara (%)	15.1 ± 0.1	36.6 ± 0.3	37.9 ± 0.1	18.8 ± 0.2	45.2 ± 0.1	40.9 ± 2.6
Xyl (%)	65.7 ± 0.5	53.1 ± 0.6	61.2 ± 0.2	65.4 ± 0.3	52.3 ± 0.3	58.3 ± 2.7
Glc (%)	17.9 ± 0.3	7.8 ± 0.9	0.3 ± 0.1	14.5 ± 0.4	1.3 ± 0.4	0.3 ± 0.0
Gal (%)	1.3 ± 0.1	2.5 ± 0.1	0.6 ± 0.2	1.3 ± 0.0	1.2 ± 0.0	0.5 ± 0.1
AX (%)[c]	80.9 ± 0.4	89.8 ± 1.0	99.1 ± 0.2	84.2 ± 0.5	97.5 ± 2.4	99.2 ± 0.1
Ara/Xyl[d]	0.2	0.7	0.6	0.3	0.9	0.7
Starch content (%)[e]	2.0 ± 0.1	3.3 ± 0.3	n.d.[e]	1.2 ± 0.0	1.2 ± 0.0	n.d.[e]
M_n (10^3 g/mol)[f]	13.4	5.1	54.2	20.0	48.8	40.9
M_w (10^3 g/mol)[f]	126.3	262.9	312.4	69.2	184.9	132.3
Dispersity index[f]	9.4	51.3	5.8	3.5	3.8	3.2
Total acetyl content (% DW)[g]	n.d.	n.d.	n.d.	34.6 ± 0.3[1]	33.1 ± 0.5[2]	36.5 ± 0.1[3]
DA[h]	n.d.	n.d.	n.d.	1.2 ± 0.0[1]	1.4 ± 0.0[2]	1.7 ± 0.0[3]
Phenolic acid content (mg g^{-1} DW)[i]	10.3 ± 0.3	n.d.	n.d.	3.8 ± 0.5	n.d.	n.d.
Ferulic acid (%)	79.0 ± 0.4	n.d.	n.d.	100 ± 0.5	n.d.	n.d.
Sinapic acid (%)	19.9 ± 0.4	n.d.	n.d.	n.d.	n.d.	n.d.
5-5AcFE (%)	1.1 ± 0.2	n.d.	n.d.	n.d.	n.d.	n.d.
EC_{50} (mg AX/mg DPPH$^{\bullet}$)[j]	17.7 ± 0.3	53.2 ± 3.9	n.a.	–	–	–

n.a. Not applicable; n.d. Not detected.
[a] The extraction yields were determined gravimetrically and calculated on the dry basis.
[b] Carbohydrate content was determined after methanolysis and TFA hydrolysis (% of total carbohydrates).
[c] Arabinoxylan (AX) content was calculated based on the total of arabinose (Ara) and xylose (Xyl) composition.
[d] Ara/Xyl is the ratio between arabinose and xylose.
[e] Starch content was calculated from the total starch kit (Megazyme). The starch content in WAX was <0.1 % according to the manufacturer.
[f] Average apparent molar masses determined by SEC using standard calibration with pullulans.
[g] Acetyl content of the whole extract. Superscript numbers: Tukey's post hoc test ($p < 0.05$).
[h] Degree of acetylation calculated as the number of hydroxyl groups substituted by acetyl groups per Ara/Xyl unit of AX. The DA was corrected based on the purity of AX. Superscript numbers: Tukey's post hoc test ($p < 0.05$).
[i] Phenolic acid content was determined after saponification followed by HPLC analysis, phenolic acid composition in % of total phenolics.
[j] The EC_{50} of ferulic acid and ascorbic acid (positive controls) was measured as 0.2 ± 0.0 and 0.1 ± 0.0, respectively.

3.2. Assessment of the chemical modification by acetylation

Acetylation was performed on the native arabinoxylans as an efficient method to introduce hydrophobicity and to reduce the water sensitivity of the derived films (Supplementary Fig. S1). The acetylated arabinoxylans (AcFAX, AcNAX and AcWAX) were characterized in terms

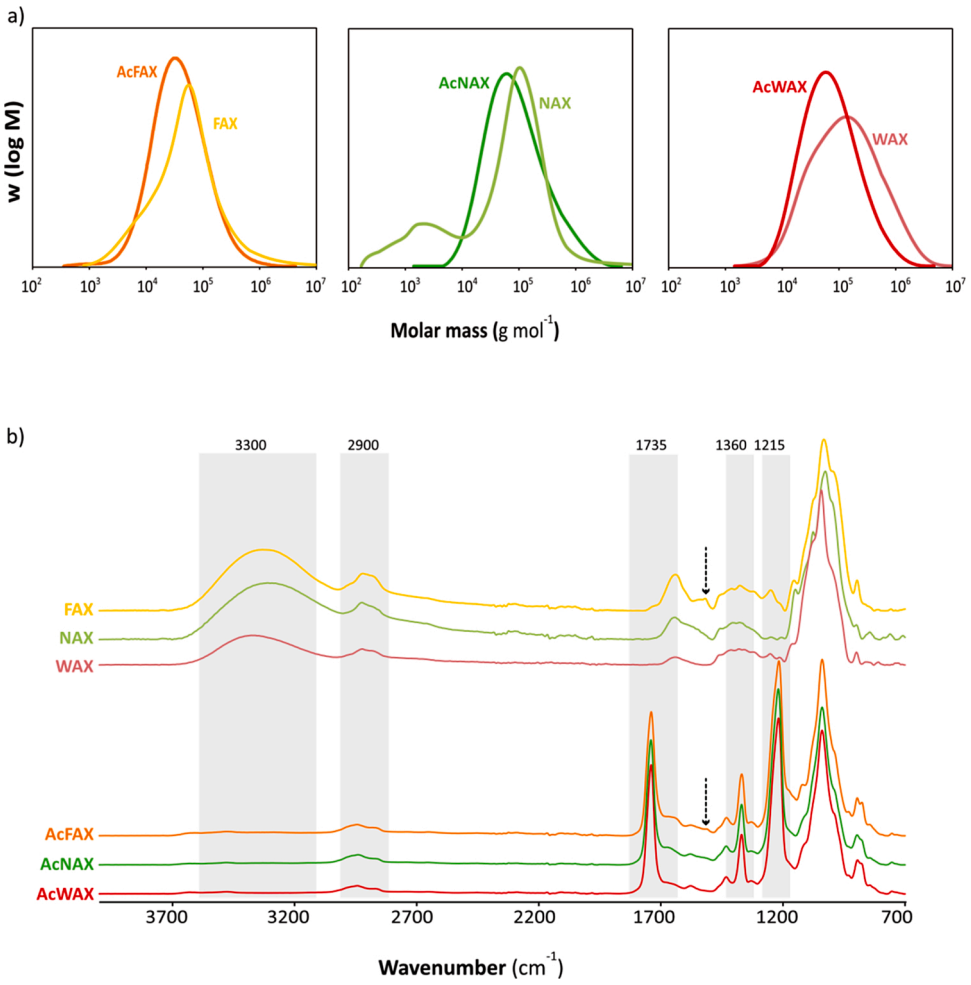

Fig. 1. a) Molar mass distribution and b) FTIR spectra of native and acetylated arabinoxylans.

of chemical composition and degree of acetylation (Table 1). The total carbohydrate content of the acetylated AXs was determined between 385.2 and 465.5 mg/g DW. As compared to the carbohydrate content of the native AXs, this decrease was explained by the introduction of acetyl groups in the carbohydrate structure (33–36 %). Another reason for this decrease could be related to the side reactions between AX and DMSO/NMI, which can introduce side groups (e.g. ketones) at the reducing ends of polysaccharides (Henniges et al., 2007; Liebner et al., 2010). The AX content of all samples was slightly enriched after acetylation, which was related to the reduction in galactose and loss in glucose that were removed by EtOH precipitation. The Ara/Xyl ratio generally remained the same after acetylation, which indicates that the chemical modification did not affect the arabinofuranosyl side groups that are more prone to hydrolysis (Sternemalm et al., 2008). After acetylation, half of the ferulic acid content in AcFAX was maintained despite the harsh conditions of the acetylation. However, the reduction in the FA content and the loss of sinapic acid and 5-5 ACFE indicated the occurrence of hydrolysis.

The two-step acetylation resulted in similar total acetyl contents in whole extracts, corresponding to the acetylation of both pentose and hexose sugars (Table 1). The introduced acetyl groups in AcFAX, AcNAX and AcWAX were statistically significantly different and measured as 34.6, 33.1 and 36.5 %, corresponding with a DA of 1.2, 1.4 and 1.7, respectively. These results indicated the different purity of samples and suggested that the higher glucose of FAX interfered with the acetylation of the AX fractions. The higher DA of WAX implied its higher reactivity as a result of its higher purity (99.2 %) and solubility. AcFAX, AcNAX and AcWAX showed monomodal molar mass distributions, confirming the homogeneous polymeric populations at $3–4 \times 10^4$, $6–7 \times 10^4$ and 6×10^4 g mol^{-1}, respectively (Fig. 1a). On the other hand, the molar mass of all acetylated AX shifted to lower values compared with the native AX fractions, indicating the occurrence of hydrolysis due to the high temperature applied for the first 5 h of acetylation. Fang, Sun, Fowler, Tomkinson, and Hill (1999) reported a similar decrease in the molecular weight of wheat straw hemicelluloses after acetylation, which was proportional to the reaction temperature employed. Interestingly, the low molar mass population observed in the alkaline extract (NAX) disappeared after acetylation and only a high molar mass fraction was observed in AcNAX. This could be explained by the potential hydrolysis during acetylation and following removal by EtOH precipitation.

FTIR analysis confirmed the successful acetylation (Fig. 1b). In the native AXs (FAX, NAX, WAX) typical spectral bands for polysaccharides were observed at 3300 cm^{-1} and 2900 cm^{-1} corresponding to the OH—stretching and the C–H stretching, respectively. The peak seen at 1630 cm^{-1} in the spectra of FAX, NAX and WAX can be ascribed to the O—H bending of absorbed water. The bands between 700 and 1500 cm^{-1} represented the fingerprint region of AX, corresponding to β-(1→4) linkages, C—OC vibration, CC and CO stretching, C———–H bending and wagging, C—OH— stretching (Robert, Marquis, Barron, Guillon, & Saulnier, 2005). In the spectra of FAX, a peak was observed at 1530 cm^{-1} (Fig. 1b, arrow), which can be attributed to the strong aromatic ring vibrations of FA (Supplementary Fig. S2). This peak was not observed in the FTIR spectra of NAX and WAX. With regards to changes after acetylation, the O—H stretching bands decreased by acetylation in all AXs as the hydroxyl groups were replaced by the acetyl groups. Moreover, the C—H stretching decreased in all three AXs and the bands

that represent the bonds related to the acetyl group increased after acetylation. These bands included the carbonyl stretching (C═O) at 1735 cm^{-1}, CC—H_3 stretching at 1360 cm^{-1} and the asymmetric stretching (C—O) of acetate at 1215 cm^{-1} (Bi, Berglund, Vilaplana, McKee, & Henriksson, 2016). In addition, the peak observed at 1510 cm^{-1} (Fig. 1b, arrow) might indicate FA as it showed a correlation with the reduced amount of FA after acetylation (Kacurakova et al., 1999).

3.3. Film-forming properties from the AX fractions and morphology

To evaluate the potential of the native and acetylated AXs for barrier applications, films were prepared by solvent casting both with and without plasticization and the material properties were analyzed. FAX did not form a continuous film without the addition of plasticizer; these poor film-forming properties can be attributed to its lower Mw and low degree of substitution (Ara/Xyl: 0.2) (Heikkinen et al., 2013). NAX and WAX formed cohesive films, enabling the characterization of material properties (Supplementary Table S2). These findings suggested that both the molar mass and the Ara/Xyl ratio are important factors determining the film formation ability of AX, indicating the challenge of tailoring material properties. The choice of extraction method appears to be the main keystone in tuning the film properties. The high substitution of AX and hence, cohesive film formation can be ensured by alkaline extraction at the expense of loss of functional groups (e.g. ferulic acid) of AX.

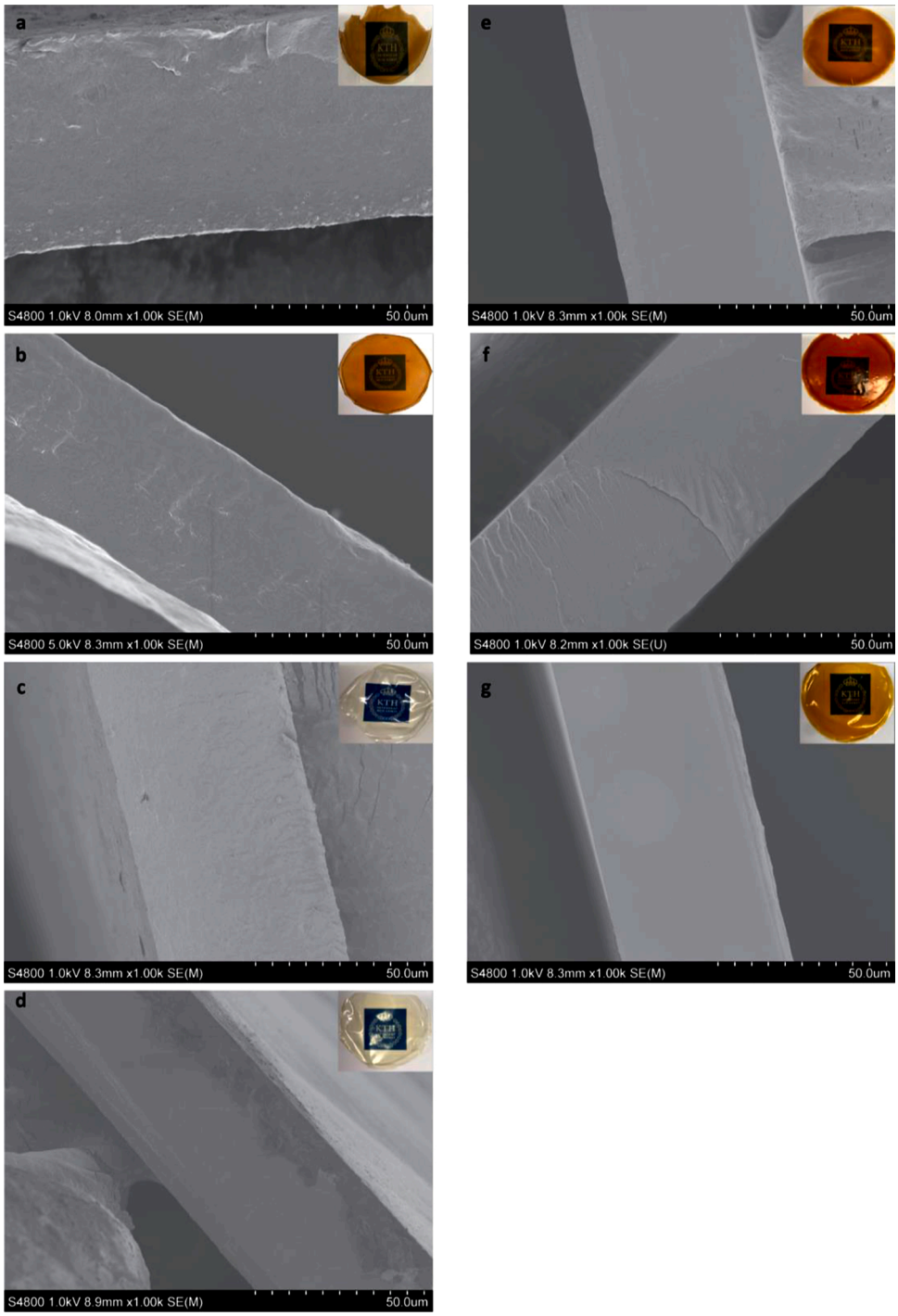

Fig. 2. Digital images of films and FE-SEM images of cross-sections of films: a) FAXSor, b) NAXSor, c) WAXSor, d) WAXSor+FA e) AcFAX, f) AcNAX, g) AcWAX.

On the other hand, AX obtained by SWE will provide bioactive films with functional properties (e.g. antioxidant activity), as discussed later. Furthermore, all the acetylated AXs without plasticization formed very brittle films (data not shown), as in agreement with Ayoub et al. (2013), possibly due to the reduced Mw after acetylation. This evidenced that acetylation does not provide sufficient internal plasticization for our AX fractions to achieve effective thermoplastic behavior. Therefore, the material properties of the non-plasticized films of the acetylated AX were not tested and not included in the following discussions. On the other hand, external plasticization resulted in continuous films for all native and acetylated AXs (Fig. 2), with thickness values between 50 and 70 μm. The films of FAXSor and NAXSor were pale brown whereas WAXSor and WAXSor+FA were colorless and transparent (Fig. 2c, d). The color of FAXSor and NAXSor could be explained respectively by the formation of degradation products and interference of lignin fragments during extraction (Reisinger et al., 2013). The plasticized films casted from all acetylated AXs were darker, indicating the side reactions between AX and the reaction medium (DMSO/NMI), i.e. the oxidation of hydroxyl groups by DMSO (Haimer et al., 2010), and the formation of colored condensed products and adducts by NMI (Liebner et al., 2010). FE-SEM imaging of the film cross-sections revealed smooth homogeneous film formation with the exception of the external FA incorporated film (WAXSor+FA). WAXSor+FA showed discontinuous zones, which may suggest the poor solubility of FA in water and hence, potential aggregation of free FA in the film network due to the saturation of hydroxyl groups in the AX chains by sorbitol (Godbillot, Dole, Joly, Roge, & Mathlouthi, 2006).

3.4. Thermal and mechanical properties of the AX films

The glass transition temperature of the films was determined by DSC analysis and presented in Table 2. The non-plasticized films of the native AXs did not show a T_g in the temperature range of the study, which was most likely due to the inherently high T_g of these amorphous polysaccharides that occurred after thermal decomposition. The T_g could only be detected when the films were plasticized and therefore, only plasticized films were included in the discussion for the thermal behavior. As shown in Fig. 3a, FAXSor and WAXSor displayed similar T_g, whereas the T_g of NAXSor was higher. This could be attributed to the presence of low molar mass fractions in NAX, which may hinder the polymer mobility of the high molar mass populations. The external incorporation of FA (WAXSor+FA) resulted in a decrease in T_g by 10 °C as compared to the non-feruloylated film (WAXSor), which may suggest that FA acted as an external plasticizer of the film (Gaudin, Lourdin, Le Botlan, Ilari, & Colonna, 1999).

As for the acetylated AX-films, the T_g decreased after the acetylation and all three acetylated AX-films showed similar thermal behavior. The T_g of AcFAX, AcNAX and AcWAX was below room temperature as hydrogen bonding was greatly restricted by the introduced acetyl groups. Indeed, the acetylation of AX reduced the T_g by 20−30 K as compared to the sorbitol-plasticized films, by seemingly inducing an internal plasticization mechanism. Additionally, the effect of triacetin should be noted in the lowered T_g. It appeared that the internal plasticization by acetylation and the external plasticization by triacetin added up to each other and further decreased the T_g by hindering hydrogen bonding and promoting chain mobility.

The thermal behavior and stability of all plasticized (Fig. 3b and Table 2) and non-plasticized films (Supplementary Table S2 and Fig. S3) was assessed using thermogravimetric analysis (TGA). The sorbitol plasticized films showed two mass loss regions corresponding to the loss of the absorbed water between 25 and 150 °C and the main thermal decomposition of the polymeric AX chains 180 and 600 °C. The presence of sorbitol in the films shifted the initiation of the thermal decomposition (T_{onset}) to somewhat lower temperatures compared to the non-plasticized films, indicating a decrease in the thermal stability due to the plasticization. The thermal decomposition of FAXSor started at 230 °C, whereas NAXSor and WAXSor started to thermally decompose, respectively, at 243.7 °C and 261.6 °C. The lower thermal stability of FAXSor could be attributed to the lower molar mass and purity of FAX.

Regarding the TGA of the acetylated AX films, three mass loss regions were observed. In fact, the regions between 100 °C and 250 °C showed two overlapping peaks. The first mass loss region (100 °C–160 °C) was attributed to the evaporation of the residual solvent (acetylacetone) used during the film preparation, whereas the second region (160 °C–250 °C) corresponded to the evaporation/decomposition of triacetin (Supplementary Fig. S4). The third mass loss region between 300 °C and 600 °C was ascribed to the main decomposition of the acetylated AX. The thermal stability of the AXs after acetylation showed a remarkable improvement regardless of the AX type. AcNAX showed somewhat lower T_{onset} compared to AcFAX and AcWAX, which was most likely related to its lower total acetyl content. As previously reported, acetylation limits intramolecular dehydration of polysaccharides by reducing the hydroxyl groups (Aburto et al., 1999; Fundador, Enomoto-Rogers, Takemura, & Iwata, 2012), which, in turn, delays the initiation of thermal

Table 2
Influence of extraction technique, ferulic acid incorporation and chemical acetylation on the thermal and mechanical properties of arabinoxylan films.

	Thermogravimetric properties					Calorimetric properties Glass transition	Mechanical properties		
	Region I*		Region II**						
	Mass loss (%)	T_{max} (°C)	T_{onset} (°C)	Mass loss (%)	T_{max} (°C)	T_g (°C)	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)
FAXSor	5.5 ± 0.1^{a}	88.3 ± 3.9^{a,c}	230.0 ± 0.2^{a}	75.7 ± 0.6^{a,c}	293.3 ± 3.2^{a,b}	31.3 ± 1.8^{a}	7.0 ± 1.6^{a}	12.9 ± 2.3^{a}	283.5 ± 50.6^{a}
NAXSor	7.8 ± 0.1^{b}	102.5 ± 0.5^{b}	243.7 ± 0.9^{b}	65.6 ± 0.1^{b}	284.2 ± 0.8^{a}	44.7 ± 0.3^{b}	26.7 ± 3.1^{b}	17.0 ± 1.5^{a}	752.0 ± 127.2^{b}
WAXSor	4.3 ± 0.2^{c}	91.6 ± 0.6^{a}	261.6 ± 0.4^{c}	76.9 ± 0.6^{a}	297.2 ± 0.0^{b}	33.6 ± 0.5^{a}	47.2 ± 4.3^{c,d}	42.3 ± 6.8^{c}	1090.5 ± 42.2^{c}
WAXSor+FA	6.6 ± 0.4^{a,b}	84.0 ± 2.2^{c}	272.0 ± 0.9^{d}	74.4 ± 0.1^{c}	295.9 ± 0.5^{b}	23.6 ± 1.5^{c}	39.0 ± 6.6^{b,c}	43.6 ± 7.5^{c}	760.0 ± 64.5^{b,c}
AcFAX	34.7 ± 0.1^{d,e}	146.6 ± 1.8^{d}	333.2 ± 1.2^{e}	53.7 ± 1.3^{d,e}	361.7 ± 1.6^{c}	22.4 ± 4.4^{c,d}	11.0 ± 0.5^{a}	9.6 ± 2.1^{a,b}	365.3 ± 69.6^{a}
AcNAX	36.4 ± 1.2^{d}	159.0 ± 0.3^{e}	322.4 ± 1.4^{f}	50.8 ± 0.9^{d}	351.3 ± 0.7^{d}	18.1 ± 0.7^{d}	10.3 ± 2.7^{a}	7.2 ± 3.0^{a,b}	318.3 ± 104.1^{a}
AcWAX	33.8 ± 0.3^{e}	163.2 ± 0.4^{f}	330.2 ± 0.3^{e}	56.2 ± 0.1^{e}	351.8 ± 1.1^{d}	19.3 ± 0.4^{c,d}	11.2 ± 2.2^{a}	17.2 ± 3.5^{b}	252.9 ± 67.1^{a}

* Region I corresponded to 25−150 °C for the native AX films and to 25−300 °C for the acetylated AX films.
** Region II corresponded to 150−600 °C for the native AX films and to 300−600 °C for the acetylated AX films, Superscript letters: Results with different letter have statistical differences ($p < 0.05$); thermogravimetric and calorimetric properties - average of duplicates and *t*-test, mechanical properties – average of 5–6 replicates and Tukey's post hoc test.

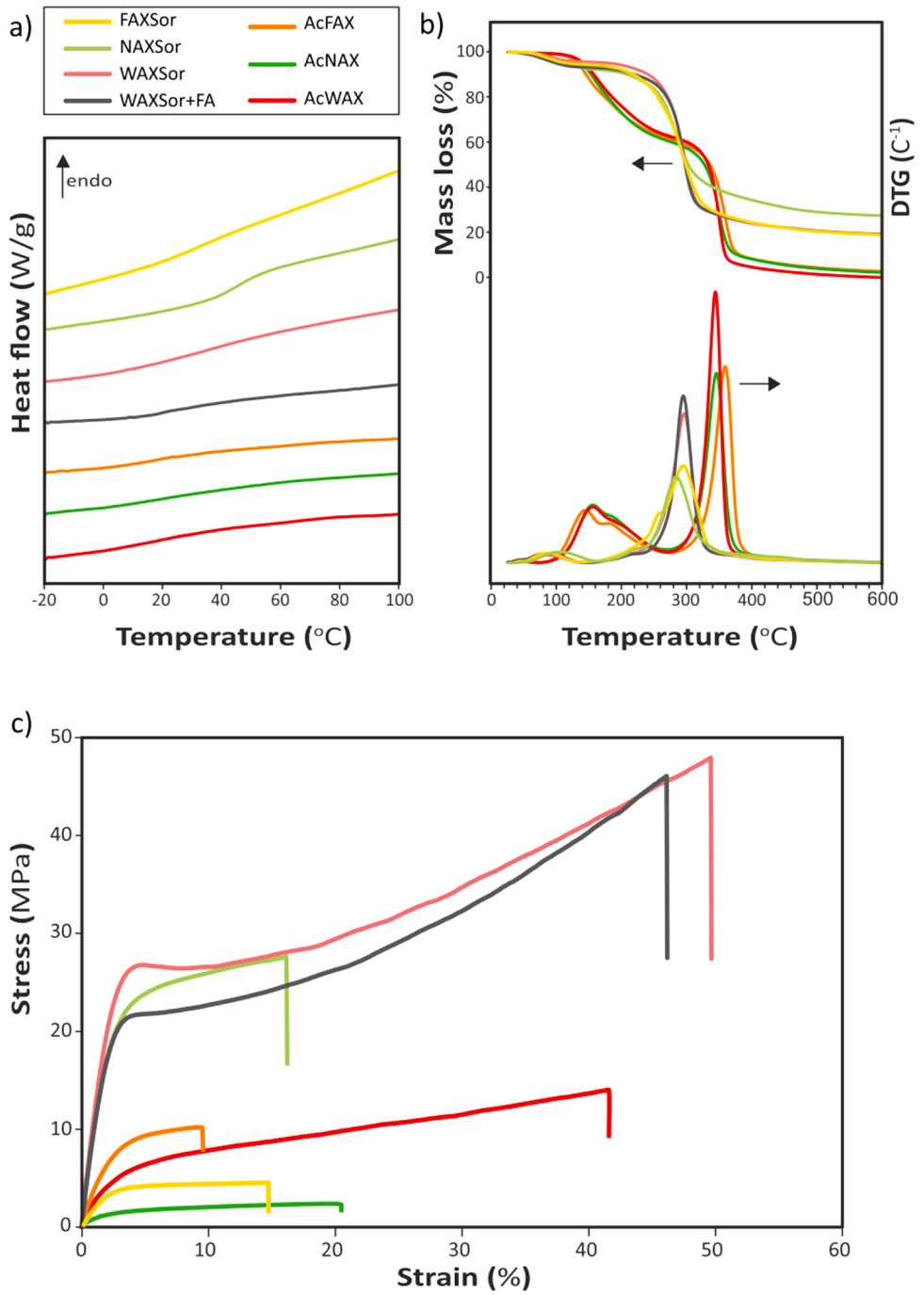

Fig. 3. Thermal and mechanical properties of arabinoxylan films. (a) DSC curve of films (T_g was determined from the 2nd heating scan), (b) TG (upper) and DTG (lower) curves of films, (c) Stress-strain curve of films.

decomposition. Similar results have been reported for acetylated xylan films from corncob and birch (Egues et al., 2014; Morais de Carvalho, Marchand et al., 2019).

The mechanical properties of all films were determined under tension, and the tensile strength, elongation at break and Young's modulus were determined from the stress-strain curves of each film (Fig. 3c and Table 2). The non-plasticized films of the native AXs were brittle and stiff, represented by the low tensile strength and high Young's modulus (Supplementary Table S2 and Fig. S5). Amongst the sorbitol-plasticized films, FAXSor displayed the lowest values of tensile strength, elongation at break and Young's modulus compared to the other AXs (Table 2). This could be attributed to the intrinsic properties of the AX fractions, i.e. molecular weight, AX purity, presence of low molar mass populations, and Ara/Xyl ratio, as the same amount of sorbitol was used in these films. The poor mechanical properties of FAXSor were seemingly related to the low Ara/Xyl ratio and slightly lower molar mass of FAX obtained by SWE. As reported in earlier studies, a high degree of arabinose substitution (Ara/Xyl ratio) has beneficial effects on the tensile strength and stiffness of AX materials, since it hinders the intermolecular interactions between xylan chains, preventing the chain agglomeration and the formation of so-called stress concentration points (Heikkinen et al., 2013; Hoije, Sternemalm, Heikkinen, Tenkanen, & Gatenholm, 2008). Correspondingly, the high Ara/Xyl ratio of NAX and WAX, together with higher Mw, yielded higher tensile strength of NAXSor and WAXSor. Surprisingly, NAXSor had much lower tensile strength and Young's modulus than WAXSor, which was incompatible with the similar Mw of

NAX and WAX. This was attributed to the lower purity and interfering effect of the low molar mass populations in NAX, which seemed to disrupt the plasticizing effect of sorbitol on the high molar mass populations (Figs. 1a and 3 c). The external FA incorporation into the film network (WAXSor+FA) decreased the tensile properties compared to the reference WAXSor film, which suggested low compatibility between FA and WAX and was also in agreement with the FE-SEM micrographs. The films of AcFAX, AcNAX and AcWAX showed similar values of tensile strength, whereas the AcWAX film showed higher values of elongation at break and Young's modulus. Previous studies have reported similar elongation at break values for non-plasticized films of acetylated AX however, the tensile strength and Young's modulus values were much higher than those of our externally plasticized films (Egues et al., 2014; Stepan, Höije, Schols, de Waard, & Gatenholm, 2012). This suggested that, in the case of acetylated films, the intrinsic differences in the molar mass distributions and/or Ara/Xyl ratio do not influence as much the mechanical performance, and instead, DA is the main determinant factor influencing the tensile properties of these films. In addition, the similar molar mass of AcFAX, AcNAX and AcWAX (Fig. 1a), which was reduced after acetylation, could be another reason for the poor mechanical properties of all the acetylated films.

3.5. Permeability and radical scavenging performance of wheat bran AX films

The oxygen permeability (OP) and water vapor permeability (WVP) of the native and acetylated AX films were measured to assess their potential as barrier materials (Table 3). All sorbitol-plasticized films showed similar OP values between 0.7–1.0 cm^3 μm m^{-2} d^{-1} kPa^{-1}. The differences between the native AXs in terms of intrinsic properties (i.e. molecular weight distribution, Ara/Xyl ratio) or the external addition of FA (WAXSor+FA) did not affect substantially the OP of the films. Regarding the AcFAX, AcNAX and AcWAX films, the OP values of these films were much higher than that of the native AX films. This was purely due to the loss of hydrogen bonding after acetylation, which disrupted the dense packing of the AX chains thereby increasing oxygen permeation.

The WVP of the sorbitol-plasticized films were remarkably low with values between 0.7 and 1.6 g mm kPa^{-1} m^{-2} d^{-1} compared to the non-plasticized films (Supplementary Table S2). This was ascribed to the formation of hydrogen bonds between sorbitol and hydroxyl groups of AXs, leading to a lower affinity towards water. Similarly, Mikkonen et al. (2009) and Zhang and Whistler (2004) have reported very low WVP by sorbitol plasticization of AX-based films. The films of AcFAX, AcNAX and AcWAX had WVP values as 4.2, 1.9 and 2.8 g mm kPa^{-1} m^{-2} d^{-1}, respectively. As expected, the WVP of these films was significantly lower than the corresponding non-plasticized films of the native AXs (Supplementary Table S2). This was related with the replacement of the hydroxyl groups with non-polar acetate groups that reduced the water affinity of the films (Koch, Johansson, Johansson, & Svegmark, 2014). However, the AcFAX, AcNAX and AcWAX films unexpectedly showed higher WVP than that of the sorbitol-plasticized AX films, despite the acetylation. These results suggest that plasticization by sorbitol is a more suitable strategy to improve barrier properties of films towards moisture compared with acetylation.

Table 3
Influence of extraction technique, ferulic acid incorporation and chemical acetylation on the radical scavenging and barrier properties of plasticized arabinoxylan films.

	EC_{50} (mg film/mg DPPH)	WVP (g mm/kPa m^2 d)	OP (cm^3 μm/m^2 d kPa)
FAXSor	13.3 ± 0.5[a]	0.9 ± 0.2[a]	1.0 ± 0.2[a]
NAXSor	43.8 ± 4.1[b]	0.7 ± 0.3[a]	0.8 ± 0.1[a]
WAXSor	n.a.	1.4 ± 0.1[a]	0.9 ± 0.2[a]
WAXSor+FA	n.a.	1.6 ± 0.2[a]	0.7*
AcFAX	n.d.	4.2 ± 1.0[b]	78.6*
AcNAX	n.d.	1.9 ± 0.4[a,b]	154.9*
AcWAX	n.d.	2.8 ± 0.2[b]	101.5 ± 23.7[b]

n.a. Not applicable; n.d. Not determined; * Only one successful measurement. Superscript letters: Results with different letters have statistical differences (*t*-test, $p < 0.05$).

The radical scavenging activity of the AX films against DPPH• radical was evaluated in terms of their EC_{50} values (Table 3). The radical scavenging activity of the acetylated AX films could not be determined as these films were not soluble in water or methanol. As expected, FAXSor and NAXSor presented similar DPPH• scavenging activity as the respective extracts (Table 1) and WAXSor did not show any activity. In addition, the EC_{50} of the non-plasticized films was similar to the native AX and the plasticized films (Supplementary Table S2). As expected, the external incorporation of free FA into the film matrix conferred DPPH• scavenging activity to the WAXSor and WAX films. Interestingly, the WAXSor+FA films never achieved a 50 % reduction in the initial DPPH• concentration (Supplementary Fig. S6), which evidences the lower radical scavenging potency of unbound FA against DPPH• compared to similar amounts of bound FA in the FAX films. Indeed, the major contributors to the DPPH• scavenging activity of cereals seem to be bound phenolic acids (Liyana-Pathirana & Shahidi, 2006; Pang et al., 2018; Yang, Dang, & Fan, 2018), although the exact mechanism behind this phenomenon is yet not well understood.

Previous studies have reported considerable improvements in the antioxidant activity of packaging films by adding FA into the film network. For example, Cheng, Wang, and Weng (2015) have reported 25–35 fold increase in the DPPH• radical scavenging activity of zein-chitosan composite films when FA (25 %, w/w) was added. However, the amount of FA in the mentioned study was much higher compared to our study, which indicates that unbound FA might be potent against DPPH• when used only in high concentrations. On the contrary, the ester-bound FA showed a strong antioxidant activity even in low concentrations as in the film from FAX in our study.

Taken together, our study demonstrates that feruloylated AX extracted via subcritical water from wheat bran constitutes a promising biomass matrix to develop multifunctional packaging films with strong antioxidant potential. These films could be particularly interesting for the packaging of foods that are prone to oxidative deterioration such as fruits, nuts and oilseeds. Food packaging requires specific material properties to protect foodstuff from physical (e.g. vibrations), chemical (e.g. oxidation) and biological (e.g. microbial growth) changes (Mikkonen & Tenkanen, 2012). In this regard, the films developed in our study offer a versatile alternative for their use in food packaging not only as stand-alone films but also in combination with other polymeric materials in multilayer packaging. The structure elucidation of the films obtained from different AX fractions in the present study suggests that chemical fine-tuning can be a useful tool to develop materials with specific properties for certain active packaging applications.

4. Conclusions

Feruloylated AX were isolated from wheat bran using subcritical water and compared with alkaline-extracted non-feruloylated AX from wheat bran and a reference wheat endosperm AX. The chemical modification of feruloylated and non-feruloylated AXs was achieved by acetylation to high degrees. The material properties of films prepared from the native and the acetylated AXs were dependent on the intrinsic features of the AX fractions, including the molecular weight, degree of substitution (DS), as well as plasticization. High molecular weight and DS of AX led to better mechanical strength and thermal stability of films. The water vapor barrier properties of the films were greatly improved by sorbitol plasticization. The use of plasticizers, therefore, could be a simple choice to obtain AX films with good barrier and mechanical properties without the need for chemical modification. The acetylation of AXs improved the thermal stability of the films but did not

substantially influence the mechanical performance and the permeability properties. The presence of bound FA in the subcritical water extracted AXs rendered films with great antioxidant capacity in comparison with the alkaline extracted and the wheat endosperm AXs. External addition of free FA slightly restored the antioxidant activity of the films, but to a lower extent than bound feruloylated AX with a similar FA content. This study demonstrates the potential of feruloylated AXs extracted from wheat bran as bio-based matrix for the design of food-packaging films with tunable material properties and radical scavenging properties, where additional functionalities towards the preservation of oxidation-sensitive foodstuff are required.

CRediT authorship contribution statement

Secil Yilmaz-Turan: Conceptualization, Investigation, Formal analysis, Visualization, Writing - original draft. **Amparo Jiménez-Quero:** Formal analysis, Supervision, Writing - review & editing. **Carolin Menzel:** Formal analysis, Writing - review & editing. **Danila Morais de Carvalho:** Investigation, Formal analysis, Writing - review & editing. **Mikael E. Lindström:** Supervision, Writing - review & editing. **Olena Sevastyanova:** Supervision, Writing - review & editing. **Rosana Moriana:** Formal analysis, Supervision, Writing - review & editing. **Francisco Vilaplana:** Conceptualization, Supervision, Writing - review & editing, Project administration, Funding acquisition.

Acknowledgments

This study was supported by the Swedish Research Council Formas (Project 942-2016-119) and the Lantmännen Research Foundation (Project 2016F008). Dr. Balázs Imre (KTH) and Dr. Annelie Moldin (Lantmännen) are acknowledged for valuable discussions.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.carbpol.2020.116916.

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