Comparison of two wheat bran extracts in the sheet extrusion process

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ABSTRACT

In this study the applicability of two differently purified crude wheat bran extracts for sheet manufacturing was evaluated. The sheet extrusion was chosen for material production because it is an industrially feasible large-scale process. The wheat bran extracts had different starch (45% and 11%) and protein (18% and 38%) contents but similar arabinoxylan (16% and 17%) and lignin (11% and 12%) contents. Glycerol, sorbitol, and their blends were used as external polyol plasticizers to enhance the continuous formation of the sheet during the process. With the chosen extrusion parameters, cohesive 100-mm-wide sheets were successfully produced with single screw extruder. The mechanical and thermal properties of the sheets were evaluated, as well as their water sensitivity. Sorbitol plasticization made the sheets stronger and stiffer and significantly lowered the watervapor permeability (WVP) and watervapor sorption (WVS) of the sheets as compared to glycerol plasticization. The sheets rich in starch had a higher tensile strength and elongation at break and a lower WVP and WVS than sheets with low starch content and high protein content. The strongest and stiffest sheet with the lowest WVP was the sorbitol-plasticized sheet with high starch and low protein content.

1. Introduction

Wheat (*Tritium* spp.) is widely cultivated in the world, and its processing produces large amounts of by-products, such as bran and straw, which are a substantial reservoir of biopolymers. Wheat bran contains up to 30% arabinoxylan (AX), approximately 20% starch, and 12–20% proteins (Bataillon et al., 1998; Hollmann and Lindhauer, 2005; Ebringerová, 2006; Xie et al., 2008; Jacquemin et al., 2015). All of these biopolymers form films individually and could be utilized more efficiently than they are currently being used, for example, in biodegradable packaging and coatings. Biopolymer films are usually produced in a laboratory scale via solution casting method onto Petri/Teflon dishes. Depending on their structural features, such as molecular weight, they may require an external plasticizer to enhance cohesive film formation. In addition, with external plasticization film properties, such as the flexibility of the film can be adjusted. Cereal-based AX has been used in various film studies, either with or without external plasticization. For example, oat spelt AX films were successfully formed when plasticized with glycerol, sorbitol, or their blends (Heikkinen et al., 2014; Mikkonen et al., 2009), whereas barley husk AX formed cohesive but brittle films without plasticization (Höije et al., 2005). Glycerol and sorbitol are often used polyol plasticizers in starch and protein films (McHugh and Krochta 1994; Talja et al., 2008). Although casting is a widely used technique on a laboratory scale, it has hardly ever been scaled up and is difficult to carry out continuously. Unlike casting, extrusion is a continuous process used to make films/sheets from biopolymers. Film extrusion of polysaccharides has been reported; corn cob arabinoglucuronoxylan, starch, pectin, and sugar beet pulp have been successfully utilized in sheet extrusion (Fishman et al., 2000, 2004; Rouilly et al., 2009; Bahcegul et al., 2013; Hietala et al., 2013; Akkus et al., 2014). In addition, sunflower protein isolate and soy protein films have been produced by extrusion (Zhang et al., 2001; Rouilly et al., 2006). Crude biopolymer fractions can be a feasible choice in film production and even enhance the film's material properties. A study with wood hydrolysate demonstrated that high-level purification is not always required; instead, crude hydrolysates may work as well as the upgraded fractions (Saadatmand et al., 2013).

The extraction of wheat bran and straw mixture using twin-screw extrusion has been reported in a recent work (Jacquemin

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Table 1
Main components and monosaccharide composition of the wheat bran extracts shown as a percentage of the dry matter (Jacquemin et al., 2015).

	WBE-S	WBE-P
Protein	17.9	38.2
Lignin	11.0	11.9
Total carbohydrates:	61.8	29.8
Arabinose	5.1	5.7
Xylose	11.0	11.5
Mannose	0.4	0.2
Galactose	0.8	1.0
Glucose	44.5[a]	11.4
Ara/Xyl	0.46	0.50

[a] Origin of glucose mainly starch.

et al., 2015). Here, we present the further processing of two of these extracts via single screw extrusion in an attempt to obtain continuous 100-mm-wide sheets. The composition of the extracts varied in terms of their starch and protein content, whereas the arabinoxylan and lignin content remained similar. The effects of both the extract composition and the external plasticizer on the mechanical and thermal properties, as well as water sensitivity, were evaluated.

2. Materials and methods

A twin screw extrusion fractionation process was used in the production of the two wheat bran extracts, one with high starch content (WBE-S) and another with high protein content and low starch content (WBE-P) (Jacquemin et al., 2015). Prior to the extraction, bran for WBE-S was de-starched by washing the bran with 40 °C water, and bran for WBE-P was de-starched enzymatically using α-amylase (BAN 480L, Novozyme, Denmark). The main components and monosaccharide compositions of the extracts are shown in Table 1 (Jacquemin et al., 2015).

Prior to sheet extrusion, the dried extracts were mixed with external plasticizers, water (30%, w/w of dry extract) and polyol (30%, w/w of dry extract), in a Perrier 32.00 mixer (Montrouge, France) to enhance cohesive sheet production in the extrusion process. Glycerol, sorbitol, and their blends (2:1, 1:1, and 1:2) were the polyols used in this study. Due to limited availability of WBE-S isolate, only 1:1 blend was tested. The mixture was stored in hermetically sealed bags at 4 °C for 12 h prior extrusion. The sheets were extruded using a Polylab Haake system (Karlsruhe, Germany) with a single-screw mechanism. The diameter of the screw was 18 mm, the screw speed was 100 rpm, and the compression rate was 1.8. The barrel temperature was adjusted as 50 °C/80 °C/100 °C/110 °C (die). The system was fitted with a 100-mm-wide sheet die with a 250 μm slit thickness. After sheet extrusion, the samples were stored at 25 °C RH 60% prior to measurements, except the samples for the water vapor sorption study, which were stored at 23 °C RH 0% (P_2O_5). The thickness of the sheets was measured at five points by using a digital micrometer (Mitutoyo, Japan) with an accuracy of 0.001 mm, and the average value was calculated.

The tensile properties of the sheets were determined with a H5KT (JFC, France) universal testing machine fitted with a 100 N load cell. At least ten specimens (75 mm long and 5 mm wide, according to ISO 527-2, type 1BA) were tested for each kind of film. The grip separation and the crosshead speed were set to 55 mm and 1 mm/s, respectively.

Dynamic mechanical analysis (DMA) experiments were performed using a Tritec 2000 DMA instrument (Triton Technology Ltd., UK) in single-cantilever bending mode. From the sheet samples, pieces of about 30 mm in length and 5 mm in width were cut, after which they were placed in a 'pocket' designed for biomaterials to be investigated by DMA. The temperature was ramped from −100 to 100 °C at 2 °C/min, with an applied frequency of 1 and 10 Hz and amplitude of 0.05 mm. The tan δ was plotted as a function of temperature in order to determine the thermal relaxations, of which the α-relaxation was taken as a glass transition.

Fig. 1. Sheet production from plasticized wheat bran extract via extrusion. Width of the die is 100 mm and slit thickness 250 μm.

In water vapor permeability measurements, sheet specimens were clamped on 6.4-cm-radius aluminum cups containing 7 g of $CaCl_2$ (RH 0%) as a desiccant. The cups were then placed in a climate room with a controlled atmosphere (25 °C and RH 60%) and weighed once a day for 7–10 days. The water vapor transfer rate (WVTR) and water vapor permeability (WVP) were calculated as described earlier (Heikkinen et al., 2013). Three parallel samples were tested for each sheet type.

A DVS intrinsic sorption microbalance (Surface Measurement Systems, Alperton, UK) was used for the water vapor sorption study, as described previously (Heikkinen et al., 2013). The measurements were carried out at a humidity range of 0–90% at 25 °C. Two parallel samples were tested.

3. Results and discussion

With both studied extracts (WBE-S and WBE-P) plasticized with polyol, 100-mm-wide continuous sheets were successfully produced by single-screw extrusion (Fig. 1). The thickness of the sheets varied, with the average values being between 280 μm to 655 μm. The thickness was larger than the slit of the extrusion die, which was caused by the expansion of the material at the extruder output. In pre-tests, slit thicknesses of 100, 250, and 400 μm were tested, and the most regular and continuous sheets were obtained with a slit thickness of 250 μm, regardless of the screw rotation speed used (75, 100, and 125 rpm). For traditional thermoplastics, low thicknesses are achieved by using post-extrusion treatments, such as blowing or calendaring, which are rarely possible with natural

Table 2
Effect of plasticizer and extract type on the mechanical properties and water vapor permeability of extruded sheets.

Plasticizer	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)	WVP (g mm/m^2 d kPa)	T_{g1} (°C)	T_{g2} (°C)
WBE-S						
Gly 30%	7.3 ± 0.5	7.4 ± 2.8	222 ± 25	28.8 ± 0.4	−59.9	+9.1
Gly 15% Sor 15%	7.8 ± 1.9	4.9 ± 1.9	168 ± 38	10.5 ± 0.1		
Sor 30%	20.7 ± 2.6	2.2 ± 0.5	736 ± 59	3.2 ± 0.1	−21.2	+33.5
WBE-P						
Gly 30%	2.4 ± 0.6	3.1 ± 1.3	84 ± 18	34.8 ± 0.4	−56.9	+3.6
Gly 20% Sor 10%	3.2 ± 0.7	2.3 ± 0.5	149 ± 3	19.9 ± 0.4		
Gly 15% Sor 15%	2.9 ± 0.9	2.2 ± 0.6	138 ± 54	21.7 ± 0.6		
Gly 10% Sor 20%	3.3 ± 1.0	2.9 ± 0.8	137 ± 51	15.3 ± 0.3		
Sor 30%	5.3 ± 1.3	1.9 ± 0.6	297 ± 32	8.7 ± 0.1	−20.7	+33.3

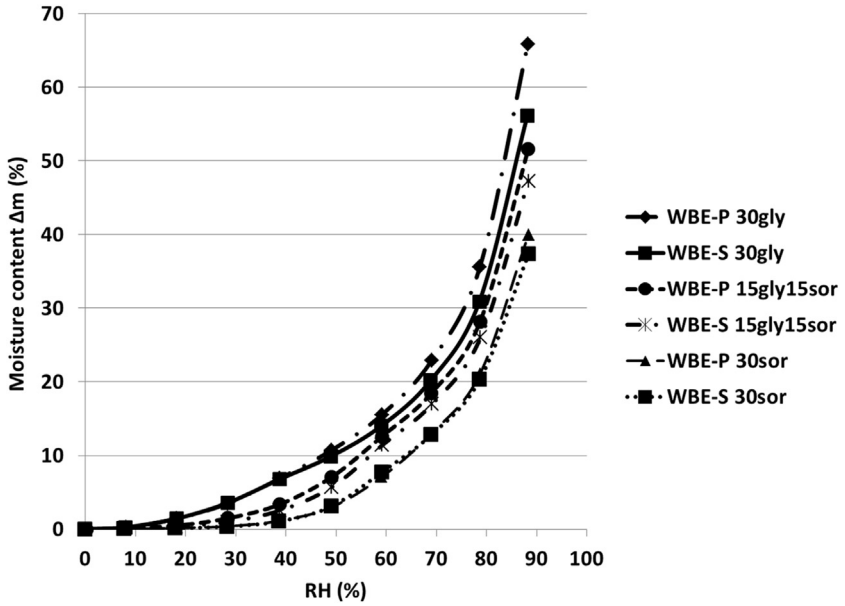

Fig. 2. Water vapor sorption of the plasticized sheets produced from wheat bran extracts (WBE) at RT. WBE-S contained higher amounts of starch and lower amounts of protein than WBE-P.

polymers due to their poor melt strengths in the extrusion conditions. Blowing has been successfully used with corn starch blends and milk caseinates (Belyamani et al., 2014; López et al., 2013). The effect of cutting direction on the mechanical properties of the sample specimens was tested with glycerol- and sorbitol-plasticized sheets. The specimens cut in the direction of the extrusion flow had somewhat better mechanical properties than the specimens cut in the perpendicular direction because of the chain alignment at the die exit; therefore, the extrusion flow direction was chosen for the analysis of all the samples.

The tensile strengths of the sheets varied from 2.4 MPa to 20.7 MPa, depending on the plasticizer and extract type used (Table 2). Additionally, stiffness and elongation, as well as water vapor permeability (WVP), were affected by the type of polyol plasticizer used. The same effect was seen in both sheet types (Table 2). With both extracts tensile strength and Young's modulus increased and elongation at break decreased when sorbitol was used as a plasticizer instead of glycerol. When polyol blends were used, the same effect was seen with increasing sorbitol content in the blend, especially in the WBE-S sheets, but to a lesser extent in the WBE-P sheets. The effect of polyol type on the film properties has been seen earlier for example with plasticized oat spelt AX films prepared via casting (Heikkinen et al., 2014). Starch content clearly increased the strength and the stiffness of the sorbitol-plasticized sheets and decreased the WVP. In the glycerol-plasticized sheets, the effect was similar, and furthermore, elongation at break increased. The results indicate that the thermoplasticization of starch that occurs during extrusion improved the material properties. The sorbitol-plasticized sheet from WBE-S clearly had the highest tensile strength (20.7 MPa) in this study, whereas the elongation at break was similar to that seen in the WBE-P sheets plasticized with glycerol, sorbitol, or their blends (Table 2). The strongest sheet in this study had a higher tensile strength than sheets prepared from glycerol-plasticized soy protein (15.6 MPa, at RH 50% and RT), glycerol-plasticized sunflower protein isolate (6.7 MPa, at RH 60% and 25 °C), and sorbitol-plasticized potato starch (8.8 MPa, at RH 53% and RT), but it had a clearly lower elongation at break (2.2% vs. 8.8%, 46%, and 23%) (Zhang et al., 2001; Rouilly et al., 2006; Hietala et al., 2013). In contrast, corn cob AGX sheet strips produced without external polyol plasticizer were stronger and elongated more (76 MPa and 35%, at RH 50% and 23 °C) as compared to the sheets in this study (Bahcegul et al., 2013).

Water vapor sorption (WVS) was higher in the glycerol-plasticized sheets than in the sorbitol-plasticized sheets for both extract types. Starch removal increased the WVS as the glycerol-plasticized sheets (WBE-P) showed lower WVS as compared to the starch-containing sheets (WBE-S) (Fig. 1). When sorbitol was used as a plasticizer, no similar effect was observed.

The glass transitions (T_g) of the glycerol- and sorbitol-plasticized sheets were analyzed using DMA (Table 2.). In all the measurements, two separate tan δ peaks were obtained indicating two T_g values (Fig. 3). WBE-S data is shown in Fig. 2 (WBE-P showed

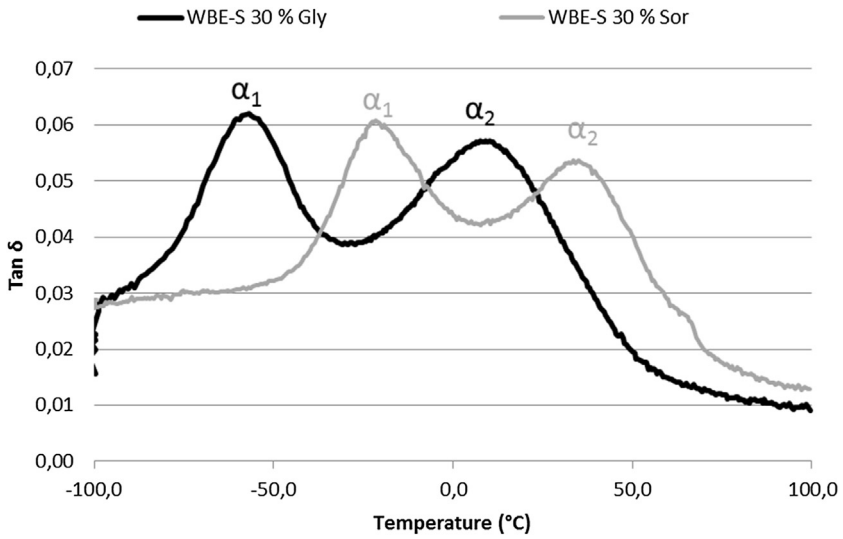

Fig. 3. Variation of tan δ for WBE-S extruded sheets plasticized with glycerol and sorbitol.

similar behavior, results not shown). It is plausible that there are separate plasticizer-rich (T_{g1}) and polymer-rich (T_{g2}) phases. The protein/starch content did not have an impact on T_g, as the values were dependent on the type of polyol rather than the extract content (Table 2). Two relaxation peaks have been observed in polysaccharide films when the phase separation of the polyol plasticizer in the film matrix occurred (Mathew and Dufresne 2002; Mikkonen et al., 2007). In this study, the extruded sheets were a mixture of arabinoxylan, lignin, protein, starch, and polyol plasticizer, and it is possible that polyol was not evenly distributed in the sheet, causing two relaxation peaks in the DMA measurements. Glycerol-plasticized extracts were in rubbery state at RT whereas sorbitol-plasticized extracts were in glassy state, explaining the highest strength and moduli, as well as the lowest WVP of the sorbitol-plasticized samples.

4. Conclusions

This study demonstrated that crude biomass extracts, such as WBEs, have potential as raw materials for sheet extrusion. The WBEs formed continuous 100-mm-wide sheets when polyol and water were added as external plasticizers. Water sensitivity and mechanical properties of the extruded sheets were affected both by the chosen polyol and the extract composition, i.e. starch content. Sorbitol plasticized WBE-S sheets had the lowest WVP and WVS. The relatively high starch content in the extract made the sorbitol plasticized WBE-S sheets stronger and stiffer compared to sheets less starch and more protein (WBE-P). The effect was similar in the glycerol-plasticized WBE-S sheets; furthermore, elongation at break increased. This result highlights the role of starch in WBEs and potential of less refined extracts in sheet preparation.

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