Mechanical Properties and Water Vapor Permeability of Thin Film from Corn Hull Arabinoxylan

Pingyi Zhang, Roy L. Whistler

Whistler Center for Carbohydrate Research and Department of Food Science, Purdue University, West Lafayette, Indiana 47907-2009

ABSTRACT: Isolated corn hull arabinoxylan was dissolved in water and provided a clear solution. Plasticizer (glycerol, propylene glycol, or sorbitol) was added to the arabinoxylan solution at 0–20 wt % (film dry weight), which was cast into stable films. Film thickness ranged from 22 to 32 μm. Mechanical properties, moisture content, and water vapor permeability (WVP) were studied for the arabinoxylan-based films as a function of plasticizer concentration. Measured data for the corn hull arabinoxylan–based films were 13–18 wt % moisture content, 10–61 MPa tensile strength, 365–1320 MPa modulus, 6–12% elongation, and $0.23–0.43 \times 10^{-10}$ g m^{-1} Pa^{-1} s^{-1} water vapor permeability. Plasticized arabinoxylan films produced in this study had lower WVPs than those of unplasticized films, which is likely attributable to the phenomenon known as antiplasticization. Scanning electron micrographs showed a homogeneous structure on film surfaces. Films containing sorbitol had the best moisture barrier properties. When grapes were coated with arabinoxylan and arabinoxylan/sorbitol films, weight loss rates of the fruit decreased by 18 and 41%, respectively, after 7 days. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 2896–2902, 2004

Key words: corn hull arabinoxylan; thin films; mechanical properties; plasticizers; coatings

INTRODUCTION

Published studies on carbohydrate films and coatings have successfully demonstrated their potential usefulness in control of moisture, oxygen, lipid, aroma, and flavor in food systems where they improve quality, safety, and product shelf life.[1–8] One useful polysaccharide group for film formation is arabinoxylans, which can be made into films of high strength and lubricity with the addition of plasticizers.[9] Arabinoxylans, a class of hemicellulose, occur in a wide variety of cereal crops.[10] Arabinoxylans constitute 50–60% of corn seed coat and are available in isolated 30–40% yield through cost-effective extraction with dilute alkali.[11] Corn hulls are byproducts from the corn-milling industry, where over 4 million tons are produced per year in the United States.[12] Currently, corn hulls have little recognized economic value ($\sim$ 0.01$/lb) and sometimes present waste-disposal problems.[13] This large quantity of residue represents a low-cost resource that could be turned into an industrial opportunity through processing into value-added products. Arabinoxylans may contribute a significant portion of human dietary fiber intake. Further advantages of this hemicellulose, as cited in the literature, are the potential health benefits of improving lipid metabolism and mineral balance,[14] improving colon function,[15] protecting against colon cancer,[16] reducing the risk of heart disease, and improving general body health.[17] Design of thin edible films and coatings with corn hull arabinoxylan may provide alternative ways for consumers to intake this potential dietary nutrient and hence would be of interest to the food industry. Objectives of this work are to develop and characterize thin edible films from isolated arabinoxylan, to examine the effect of type and concentration of plasticizers (glycerol, propylene glycol, and sorbitol) on the functional properties of the films, and to determine the ability of the arabinoxylan films to reduce moisture loss from grapes.

EXPERIMENTAL

Materials

Studies of the isolation and characterization of corn hull arabinoxylan were previously reported.[11] In brief, dried corn hulls were extracted with 4% dilute alkali and supernatants were combined, neutralized, and centrifuged. Arabinoxylan in the supernatant was precipitated, washed with ethanol, and dried. Arabinoxylan samples were then fully hydrolyzed and derivatized to alditol acetates for analysis of carbohydrate composition using gas chromatography with a mass

Correspondence to: P. Zhang (zhangp@foodsci.purdue.edu).

selective detector. Size-exclusion chromatography with multiangle laser light scattering was used to determine molecular weight and distribution of arabinoxylan. Corn amylopectin (9037-22-3; Sigma–Aldrich, Milwaukee, WI) and carboxymethyl cellulose (CMC, 9004-32-4; Sigma–Aldrich) were used as film-forming polysaccharides to compare performance with that of arabinoxylan. Polysaccharides were maintained in desiccators after drying under vacuum at 60°C to a constant weight before use in film-forming studies. Propylene glycol, glycerol, and sorbitol were purchased from Sigma–Aldrich (purity > 98%).

Arabinoxylan film formation

Corn hull arabinoxylan and corn amylopectin were each dissolved in deionized water overnight with constant stirring to give clear solutions of 7.5 wt % (film dry weight). Propylene glycol, glycerol, or sorbitol concentration of 0–22% was then added for plasticization. The solution was degassed under vacuum before casting onto glass plates (30 × 40 cm) to a thickness of 0.8 mm. CMC film was made in parallel from a 3.25 wt % solution with 1.6 mm coating thickness. Casting plates were placed on a level surface at ambient conditions until the dried film could be peeled. Dried films were then cut into test specimens and conditioned at 22°C and 54% relative humidity (RH) at least 2 days before measurements. Amylopectin films thus formed were too brittle to be peeled off the glass plates. For each formulation a minimum of two films were made and characterized by each of the following methods: scanning electron microscopy (SEM), thickness, tensile test, moisture content, water vapor permeability (WVP), and grape preservation as described in the following sections.

Scanning electron micrographs

Scanning electron micrographs were taken with a JSM-840 scanning electron microscope (JEOL, Tokyo, Japan). Film samples were mounted on 12-mm aluminum stubs and sputter-coated with gold–palladium. Magnification was ×10,000 and voltage was 5 kV.

Tensile test

Tensile strength and breaking elongation of films were measured on a Universal testing machine (MTS® Sin-Teck 10; DeFelsko Corp., Ogdensburg, NY) according to ASTM standard D 882-97.[18] At least five repeated measurements of each film were used to determine mechanical properties.

Thickness and moisture content

Film thickness was measured (PosiTector® 6000 Coating Thickness Electronic Gage, DeFelsko Corp.) to the nearest 1 μm around the film testing area at five random positions. An average of five values of film thickness was used in calculations. Water content of the films was determined by

$$\text{Moisture content (\%)} = \frac{W_0 - W_1}{W_0} \times 100 \quad (1)$$

where W_0 and W_1 are the weight of films maintained at controlled cabinet (22°C, 54% RH) for 48 h, and in an oven (80°C) to a constant weight, respectively. All samples were analyzed in duplicate.

Water vapor permeability

The cup method (ASTM E 96-95)[19] was used to determine water vapor permeability (WVP) with a 54% RH gradient at 22°C. Cups were filled with 32 g anhydrous calcium chloride (0% RH) as desiccant and film samples were mounted over the cups. The desiccant was dried at 240°C for 3–5 h before use. Cups were then placed in a 54% RH cabinet containing a saturated magnesium nitrate solution. WVP was determined by

$$\text{WVP} = \frac{(dm/dt)L}{A\Delta P} \quad (2)$$

where dm/dt, L, A, and ΔP are the slope of the weight loss versus time (g/s), film thickness (m), the film area exposed to moisture (3.167×10^{-3} m^2), and the difference of the vapor pressure between the two sides of films (1.47×10^3 Pa), respectively. For each WVP value three samples were tested.

Film-coating preservation of grapes

Commercial grapes were washed, dried in the open air, and then randomly divided into five groups with 20 fruits per group. Fruits were sprayed with water (control), 2 wt % arabinoxylan, and 2 wt % arabinoxylan/0.22 wt % sorbitol, 2 wt % corn amylopectin, and 2 wt % CMC solution for 30 s, respectively. Corn amylopectin and CMC films were used as comparisons for film coating preservation. Fruits were dried in open air for 3 h. Thin films that formed on the fruits displayed shiny surfaces. Both control and experimental samples were placed at ambient conditions (22°C and RH 40 ± 10%) for 7 days. Weight loss of the fruits was measured at 24-h intervals and was expressed by

$$\text{Weight loss (\%)} = \frac{W_0 - W_1}{W_0} \times 100 \quad (3)$$

where W_0 and W_1 are the original weight and measuring weight of the whole group after preservation,
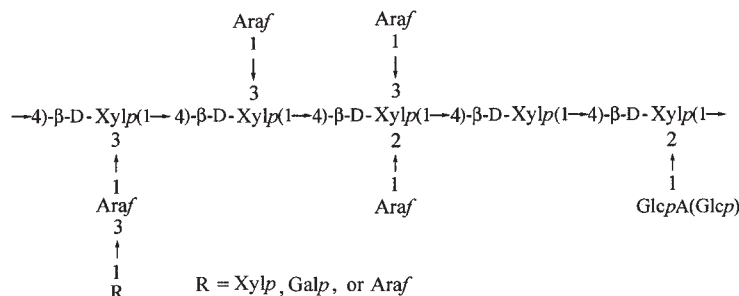
Ara*f*   Ara*f*
1   1
↓   ↓
3   3
→4)-β-D-Xyl*p*(1→ 4)-β-D-Xyl*p*(1→4)-β-D-Xyl*p*(1→4)-β-D-Xyl*p*(1→4)-β-D-Xyl*p*(1→
3   2   2
↑   ↑   ↑
1   1   1
Ara*f*   Ara*f*   Glc*p*A(Glc*p*)
3
↑
1
R   R = Xyl*p*, Gal*p*, or Ara*f*

Figure 1 Typical structure of corn hull arabinoxylan.

respectively. Experiments were performed in duplicate.

Statistics

Differences between means values were analyzed using one-way ANOVA and followed by Tukey's multiple-range tests. A value of $p < 0.05$ was considered to be statistically significant.

RESULTS AND DISCUSSION

Structure of corn hull arabinoxylan

Corn hull arabinoxylan consists of L-arabinose (30.9 mol %), D-xylose (48.6 mol %), D-galactose (6.0 mol %), and D-glucose/glucuronic acids (11.4 mol %). Weight-average molecular weight and intrinsic viscosity of arabinoxylan, as determined by light scattering and viscometry in water, were 506,000 and 174 cm^3/g, respectively.[11] Corn hull arabinoxylan has a substituted backbone of β-(1→4)- D-xylopyranosyl units with side chains of α-L-arabinofuranosyl units, attached mainly at O-3 positions, and also at O-2 positions of the D-xylose moieties (Fig. 1). There are other attached groups such as α-D-glucuronic acid residues at O-2 and D-galactose residues.[20,21] Although the backbone xylan structure is similar to that in cellulose, arabinoxylan has less driving force to produce crystalline-type structures than cellulose because of its irregularities, where the presence of side chains reduces chain interactions. However, in relatively unsubstituted regions of the xylan, the chain should be able to associate and introduce inter- and intramolecular interactions. The polymer features of corn hull arabinoxylan are responsible for its water solubility and relatively strong film-forming property.

Microstructure

Arabinoxylan films were smooth, transparent, and 22–32 μm in thickness. Figure 2 shows micrographs of the evaporation surface of arabinoxylan-based films. Both the arabinoxylan films and the plasticized arabinoxylan films display a homogeneous structure on the surface. Uniform deposition of arabinoxylan-based films may explain their surface gloss and transparency.

Mechanical properties

Mechanical property data [elastic modulus (EM), tensile strength (TS), and percentage (%) elongation] of arabinoxylan-based films are shown in Table I. Propylene glycol–plasticized films were more brittle, and mechanical properties were almost independent of plasticizer content. Increasing propylene glycol content did not produce a significant change in mechanical properties. Films containing glycerol and sorbitol exhibited negative dependency on plasticizer concentration for TS and EM, although increasing plasticizer concentration increased elongation. Glycerol- and propylene glycol–plasticized films exhibited positive dependency on plasticizer concentration for moisture content, whereas sorbitol content did not significantly modify moisture content (Fig. 3). Propylene glycol–plasticized films showed a sharp break with higher breaking force (EM = 1290–1314 MPa and TS = 52.6–60.7 MPa, respectively) and low deformation (5.9–7.9% elongation). Similar results were reported in propylene glycol–plasticized cellulose[22] and methylcellulose films[23] where propylene glycol had less effect than glycerol on film tensile strength and elongation. Glycerol and sorbitol have similar chain structures; however, glycerol is a lower molecular weight plasticizer and is more hygroscopic. It was reported that lower molecular weight plasticizers produce more film plasticization than do those of higher molecular weight.[24] This is consistent with results obtained in this study.

Water vapor permeability

Plasticizers such as glycerol, propylene glycol, and sorbitol are often used to modify the mechanical properties of a film, although these additives may cause significant changes in barrier properties, as observed
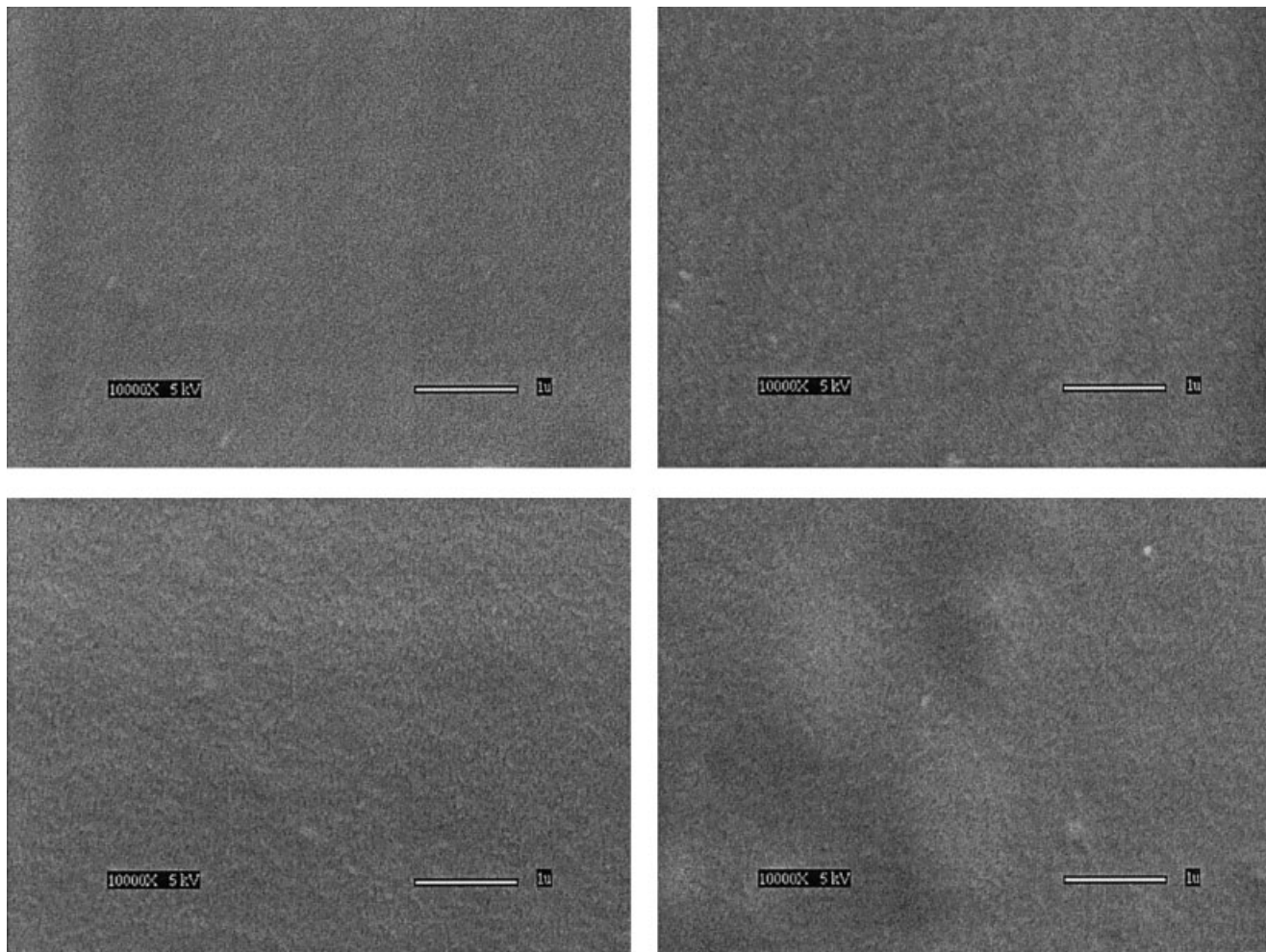
Figure 2 SEM images of the arabinoxylan (AX) films. AX (top left); AX + PG ($C_P = 0.200$, top right); AX + Gly ($C_P = 0.194$, bottom left); AX + Sor ($C_P = 0.198$, bottom right). C_P = g plasticizer/(wt plasticizer + wt arabinoxylan).

in this study (Fig. 4). Sorbitol-plasticized arabinoxylan films had the best moisture barrier properties (WVP = 0.23×10^{-10} g m^{-1} Pa^{-1} s^{-1} at $C_P = 0.128$). Glycerol- and propylene glycol–plasticized films had reduced WVP values (0.31×10^{-10} g m^{-1} Pa^{-1} s^{-1} at $C_P = 0.051$ and 0.36×10^{-10} g m^{-1} Pa^{-1} s^{-1} at $C_P = 0.163$) compared with those of unplasticized films (0.47×10^{-10} g m^{-1} Pa^{-1} s^{-1}); however, both had higher WVP than that of sorbitol-plasticized films; whereas arabinoxylan and high concentration glycerol-plasticized films were poor moisture barriers (WVP = 0.43×10^{-10} g m^{-1} Pa^{-1} s^{-1} at $C_P = 0.200$). As shown in Figure 4, the WVP curve goes up with glycerol concentration above 10%, indicating that excess glycerol and the greater amount of affinitive water improve its effectiveness to break chain-to-chain interactions, and thus introduce more free volume in the arabinoxylan film matrix.

Propylene glycol and glycerol have size and hygroscopic similarities, although propylene glycol has less effect than glycerol on mechanical properties and

WVP, which may be attributable to the lower number of hydroxyl groups available to interact with arabinoxylan. Sorbitol-plasticized films have lower WVP values than those of glycerol-plasticized films (Fig. 4), as expected from the higher tensile strength and elastic modulus values for sorbitol–arabinoxylan films compared to those of glycerol–arabinoxylan film with similar plasticizer concentration. Both results in mechanical property and WVP suggest that the bulky and poorly hygroscopic sorbitol is less able than glycerol to affect hydrogen bonding between polysaccharide chains. Results showed that glycerol-plasticized films are more flexible, and therefore likely have more free volume in the arabinoxylan matrix compared to that in the propylene glycol and sorbitol-plasticized films. Sorbitol also gives lower WVP than glycerol in protein films.[25,26]

It is quite common that increasing the level of the plasticizers would increase WVP of the films; however, all plasticized arabinoxylan films produced in this study have lower WVPs than those of unplasti-

TABLE I
Thickness, Mechanical Properties of Arabinoxylan Films with Different Plasticizer Concentrations (C_P),
and Data of Edible Films From the Literature

Film[a]	C_P[b]	Thickness (μm)[c]	Tensile Strength (MPa)[c]	Modulus (MPa)[c]	Elongation (%)[c]
AX	0	26.0 ± 0.8	53.8 ± 0.4[A]	1316 ± 90[A]	6.2 ± 1.6[A]
AX + PG	0.068	26.4 ± 1.5	53.2 ± 2.6[A]	1290 ± 126[A]	5.9 ± 0.7[A]
	0.115	23.4 ± 2.3	55.4 ± 4.9[A]	1320 ± 136[A]	6.5 ± 0.4[A]
	0.163	26.8 ± 2.6	60.7 ± 4.4[A]	1287 ± 266[A]	7.9 ± 1.1[A]
	0.194	26.3 ± 1.5	55.0 ± 5.9[A]	1225 ± 115[A]	6.6 ± 1.4[A]
	0.219	27.6 ± 3.7	52.6 ± 6.7[A]	1314 ± 197[A]	6.0 ± 0.5[A]
AX + Gly	0.027	22.3 ± 1.2	46.5 ± 3.5[B]	1148 ± 163[A]	5.6 ± 0.5[A]
	0.051	26.3 ± 1.9	35.3 ± 5.8[B]	1093 ± 55[A]	5.9 ± 0.6[A]
	0.100	24.3 ± 3.9	25.4 ± 8.1[C]	884 ± 112[B]	7.4 ± 2.6[A]
	0.146	29.8 ± 2.6	14.1 ± 1.3[C]	477 ± 60[C]	10.0 ± 2.5[B]
	0.200	28.4 ± 0.9	9.7 ± 2.9[D]	365 ± 73[D]	12.1 ± 1.5[B]
AX + Sor	0.051	25.3 ± 1.5	47.5 ± 10.9[A]	1161 ± 133[A]	5.5 ± 1.4[A]
	0.091	28.0 ± 1.0	43.7 ± 3.8[B]	1094 ± 35[A]	6.5 ± 1.0[A]
	0.128	28.0 ± 0.8	32.1 ± 8.6[C]	969 ± 131[B]	6.7 ± 1.3[A]
	0.164	32.3 ± 1.3	29.7 ± 4.1[C]	837 ± 100[B]	7.3 ± 1.1[A]
	0.198	29.5 ± 1.5	19.7 ± 4.3[C]	463 ± 90[C]	8.9 ± 1.4[A]
Corn starch[39]	—	25	46	—	2.5
Soluble starch[40]	—	50	50.5 ± 5.4	—	4.2 ± 0.5
Pullulan[41]	—	81.3 ± 2.5	34.2 ± 0.5	—	2.9 ± 0.2
Methylcellulose[42]	—	25 ± 2	20	—	1.2–1.8
Zein[43]	—	40–92	7–9	270–320	3–12
Cellophane[44]	—	—	50–120	3000	10–50

[a] At 22°C, 54% RH, arabinoxylan (AX), propylene glycol (PG), glycerol (Gly), and sorbitol (Sor).
[b] C_P = wt plasticizer/(wt plasticizer + wt arabinoxylan).
[c] Mean ± standard deviation. Values within table columns with different superscripts (A, B, C, D) are statistically significant in Tukey tests at $p < 0.05$.

cized films. Chitosan film was reported to have lowered WVPs as the level of plasticizers increased.[27] Also, plasticizers could enhance or retard WVP, depending on their concentrations in cellulose-based 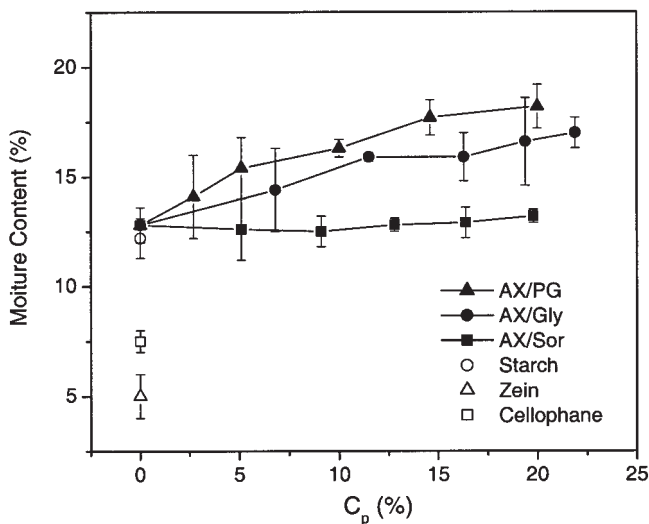films.[22,28,29] This behavior is likely attributable to the phenomenon known as antiplasticization.[30–34] Antiplasticization involves intermolecular bonding between plasticizers and the polymers, and thus reduction of molecular mobility in polymer matrix by small amounts of plasticizers would result in decreased WVPs. Addition of glycerol[30] or sorbitol[31,32] was re-
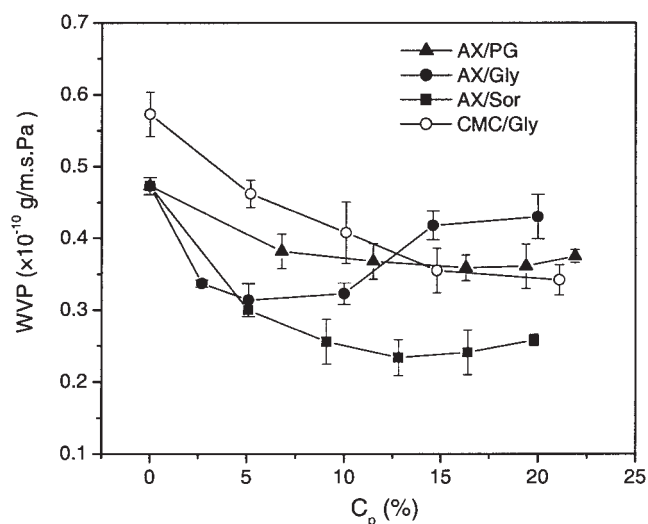

Figure 3 Moisture content of arabinoxylan films at 22°C and 54% RH and comparison with starch film,[39,40] zein film,[43] and cellophane.[44] C_P = g plasticizer/(wt plasticizer + wt arabinoxylan).

Figure 4 Water vapor permeability of arabinoxylan films at 22°C, and 54% RH. C_P = g plasticizer/(wt plasticizer + wt arabinoxylan).
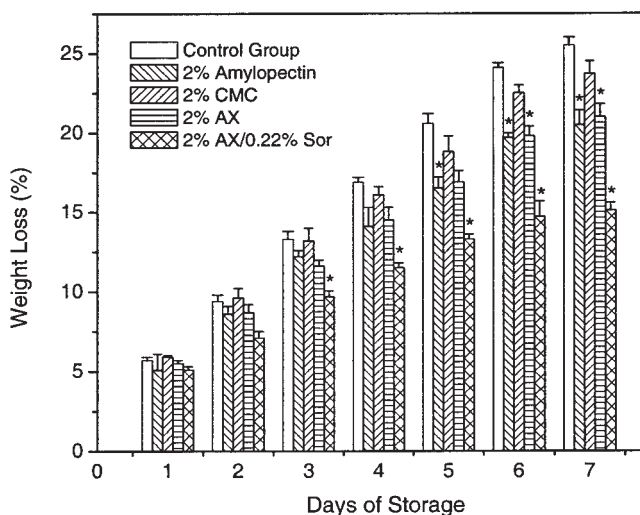
Figure 5 Weight loss rate of grapes coated with arabinoxylan films during 7-day period. *Weight losses are significantly different from control group at $p < 0.05$.

ported to avoid antiplasticization when their concentrations reached 20–25 and 21–27% in starch films, respectively.

Additionally, water vapor permeability and mechanical property data of arabinoxylan are inconsistent with the results from Peroval et al.[6] and Phan The et al.[7,8] The reason may be attributed to different film thicknesses (22–32 versus 58–91 μm), humidity gradients (0/54 versus 22/84%), draw rates at tensile testing (10 versus 100 mm/min), and different origins of corn hull arabinoxylans. It appeared that film thickness and humidity gradient significantly affect WVP values of hydrophilic films.[35,36] These differentiations make the results less comparable.

Film-coating preservation of grapes

Weight loss rates of grapes during storage (shown in Fig. 5) suggest that the weight loss rate decreased after film-coating preservation, especially for grapes coated with arabinoxylan–sorbitol (AX/Sor) films. The weight loss rate for grapes coated with AX/Sor films was significantly different from that of the control group after the third day ($p < 0.05$). Weight losses were found to be 82, 80, 93, and 59% of the control group for grapes coated with AX, corn amylopectin, CMC, and AX/Sor after 7 days of preservation, respectively. These findings demonstrate the good moisture barrier ability of sorbitol-plasticized arabinoxylan films. The film coatings on grapes could be easily washed off before serving, or the arabinoxylan-based film coatings could be eaten with the grapes as a source of dietary fiber.

Edible film coatings with moisture barrier properties can prevent deterioration and extend the shelf life

of food products.[37] Application of edible films on fruits (such as citrus products, apples, and pears) can help to prevent moisture loss and improve gloss.[5] Because 25 to 80% of harvested fresh fruits and vegetables are lost because of spoilage,[4] one method of extending postharvest shelf life could be the use of an edible film coating. Such coatings can be made of edible materials that provide a barrier to gases and water vapor. Modified internal atmosphere was reported to reduce respiration and thereby delay ripening and prolong shelf life of fruits.[38] Polysaccharide films, because of their hydrophilic nature, are generally poor moisture barriers. However, the arabinoxylan–sorbitol films used in this study significantly delayed moisture loss from grapes. Advantages of many polysaccharide films may be more in the area of gas exchange rather than retardation of water loss.[1] In the future, a coating may reduce the need for energy-intensive refrigeration and costly controlled atmosphere storage.[4]

CONCLUSIONS

Thin edible films were developed using corn hull arabinoxylan. These films were stable, strong, smooth, and transparent and had mechanical properties, moisture content, and water vapor permeability controlled by the plasticizer. Sorbitol-plasticized arabinoxylan films were good moisture barriers. All plasticized arabinoxylan films produced in this study had lower WVPs than those of unplasticized films, likely attributable to the antiplasticization effect of these plasticizers at low concentrations.

Microstructure images confirmed the fine microstructure of films and the good miscibility between arabinoxylan and the plasticizer. The film-coating preservation experiment to grapes showed that arabinoxylan-based film coatings have moisture barrier ability.

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