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Water barrier and physical properties of starch/decolorized hsian-tsao leaf gum films: Impact of surfactant lamination

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ABSTRACT

The moisture barrier and physical properties of bilayer films prepared by lamination of starch/decolorized hsian-tsao leaf gum (dHG) and surfactant layers were investigated. It was found that the water vapor permeability (WVP) of tapioca starch/dHG film (1.31×10^{-10} g/m s Pa) pronouncedly decreased by the aid of a surfactant layer lamination ($1.36–5.25 \times 10^{-12}$ g/m s Pa). The WVP of bilayer film increased with increasing the concentration of starch/dHG in the surfactant layer, but was not significantly influenced when it was thickened. The sorption isotherms of both monolayer and bilayer films made from starch/dHG showed typical behavior of water-vapor-sensitive hydrophilic biopolymers. However, the equilibrium moisture content of the monolayer film was significantly higher than that of bilayer films when water activity (a_w) reaches 0.33. Both the tensile and puncture force of starch/dHG films did not vary significantly by laminating a surfactant layer, indicating the mechanical strength of surfactant layer is relatively weak, and this surfactant layer mainly served as a barrier for moisture. When compared to emulsion-based starch/dHG films with surfactant, the surfactant laminated starch/dHG films showed higher water barrier property, mechanical strength, and transparency.

1. Introduction

Fresh-like quality, safety, and convenience of foods are the increasing requirements for consumers in modern times. Edible films or coatings function as a barrier of mass transfers (such as water vapor, gas, oil), a carrier of food ingredients and additives (such as antioxidant, antimicrobial agents, pigment), and a mechanical protection against deterioration (Debeaufort, Quezada-Gallo, & Voilley, 1998; Donhowe & Fennema, 1994; Park, 1999). Reports have shown that edible films and coatings can effectively promote the quality, shelf life, and convenience of minimally processed foods (Ayranci & Tunc, 2004; Chien, Sheu, & Yang, 2007; Debeaufort et al., 1998; Durango, Soares, & Andrade, 2006; Kristo, Biliaderis, & Zampraka, 2007; Lee, Park, Lee, & Choi, 2003; Park, 1999; Parra, Tadini, Ponce, & Lugão, 2004; Rico-Pena & Torres, 1990). Additionally, edible films and coatings are biodegradable, which makes them potentially good for food packaging, particularly in reducing the amount of plastic waste (Debeaufort et al., 1998; Parra et al., 2004; Petersen et al., 1999).

Carbohydrates (starches, pectins and other polysaccharides), proteins, lipids and combinations of these can be used to make edible films. Starch is one of the most promising natural biopolymers for edible films due to the benefits of low cost, abundance in nature, renewability, biodegradability and film-forming ability. Some studies have reported that plasticized pectin/starch films have high modulus, good mechanical properties, and excellent oxygen barrier properties; the properties of plasticized pectin/starch films by extrusion are comparable to those by casting (Coffin & Fishman, 1993, 1994; Fishman, Coffin, Konstance, & Onwulata, 2000). Hsian-tsao herb (*Mesona procumbens* Hemsl), a member of the Labiate family, has been used as one of the remedy herbs in Chinese folk medicine to alleviate heat prostration, hypertension, diabetes, and muscle and joint pain (Yen & Hung, 2000). Decolorized hsian-tsao leaf gum (dHG) is a highly ionic heteroglycan, constituted approximately 40% of uronic acid by weight, and also contains a range of neutral sugar, including mannose, rhamnose, galactose, glucose, arabinose, xylose in a decreasing order. Though the monosaccharide compositions of dHG are similar to those of pectins, its uronic acid level is lower than that of commercial pectin (generally at least 65% by weight). Furthermore, the ash content (approximately 28%) of dHG is much higher than that of pectins (Chen & Lai, 2008; Lai & Chiang, 2002; Lai & Liao, 2002a, 2002b; Lai & Lin, 2004). Chen and Lai (2008) reported that the mechanical strength of tapioca starch films could be significantly enhanced by the addition of appropriate amount of dHG. Starch/dHG films have also been shown to be a promising type of bio-films due to their

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transparent and homogeneous matrix, stable structure at ambient conditions, and reasonable water barrier property (Chen, Kuo, & Lai, 2009a; Chen & Lai, 2008).

Edible films and coatings made from hydrocolloid (carbohydrates and proteins) generally possess higher mechanical strength and gas barrier property than lipids, but they prove to be lower moisture barriers because of their hydrophilicity. To improve moisture barrier characteristic, hydrocolloid-lipid composite films, in laminated or emulsion form, have been performed to combine the mechanical strength and gas barrier property of hydrocolloid films with the good moisture barrier property of lipid. Hydrocolloid films laminated with lipids promoted moisture barrier characteristic significantly, for the continuous lipid layer could prevent moisture migration between different gradient of water vapor pressures. On the other hand, emulsion-based edible films with lipids have been shown to be 10–1000 times less efficient as a moisture barrier than bilayer films. However, emulsified films have some advantages; they need less processing steps than bilayer films and can be used at room temperature, so emulsified films are generally more favorable than bilayer films in industries (Debeaufort, Martin-Polo, & Voilley, 1993; Gallo, Debeaufort, Callegarin, & Voilley, 2000).

Surfactants are amphiphilic substances, which possess hydrophilicity and hydrophobicity simultaneously. A relatively new approach to improve the moisture barrier properties of hydrophilic films is by adding surfactants. For examples, Villalobos, Hernández-Muñoz, and Chiralt (2006) reported that the addition of surfactant mixtures (Span 60 and sucrose ester P-1570) in the film-forming solution significantly reduced the equilibrium moisture content and increased moisture barrier property of the hydroxypropyl methylcellulose (HPMC) film when a critical amount of surfactants (i.e. hydrocolloid to surfactant ratio of 0.5) were added. In contrast, Rodríguez, Osés, Ziani, and Maté (2006) reported that potato starch films with surfactants, such as Tween 20, Span 80, and lecithin, do not show significant effect on moisture barrier property, but these additives did show significant effect on mechanical properties. In our previous report (Chen, Kuo, & Lai, 2009b), we found that composite films of starch/dHG/surfactant in emulsion form showed a significant increase in moisture barrier performance, alongside a tendency to decrease in mechanical strength. Therefore, we hypothesize that surfactant/(starch/dHG) bilayer films in laminated form, made from uniform distribution of surfactant layer on the pure starch/dHG film could possibly obtain a better moisture barrier property by the aid of surfactant layer and better mechanical strength by the aid of starch/dHG layer. The objective of this study was to verify the above hypothesis. Specifically, the moisture sorption isotherms, mechanical properties, optical character, and microstructure of the bilayer films made from starch/dHG and surfactant by way of lamination would be investigated.

2. Materials and methods

2.1. Materials

Dried hsian-tsao leaves were purchased from a contracted farmer (Sanyi, Miao-Li, Taiwan). Extraction and decolorization of hsian-tso leaf gum were performed according to the method of Chen and Lai (2008). The metal ions contents in dHG were analyzed according to the method of AOAC (2005). The chemical compositions, molecular weigh and intrinsic viscosity of dHG were listed in Table 1 (Chen & Lai, 2008; Lai & Chiang, 2002; Lin, 2002). Tapioca starch (22.5 ± 0.5% amylose on a dry basis) was kindly provided by Ku-Tung Foods Inc. (Chia-Yi, Taiwan). Sucrose ester S-1170 (Hydrophilic–lipophilic balance, HLB = 11) was kindly provided by Gemfont Corporation (Taipei, Taiwan). Reagent grade glycerol was purchased from Shimakyu's Pure Chemicals (Osaka, Japan). All other reagents were in the analytical grade.

Table 1
Chemical compositions and some physical properties of decolorized hsian-tsao leaf gum.

Yield (%)[a]	3.52
Crude protein (%)[b]	0.15
Crude fat (%)[b]	0.22
Crude fiber (%)[b]	1.96
Ash (%)[b]	28.35
Na (mg/g)	40.78
K (mg/g)	50.97
Ca (mg/g)	0.49
Mg (mg/g)	0.13
Fe (mg/g)	0.18
Zn (mg/g)	0.08
NFE (Nitrogen-free extract) (%)[b]	69.54
Uronic acid (%)[b]	40.70
Neutral sugar (molar %)[c]	
Mannose	28.43
Rhamnose	23.86
Galactose	20.30
Glucose	17.77
Arabinose	5.08
Xylose	4.56
$[\eta]$ (dL/g)[a]	9.06
M_w[a]	5.5×10^5
Coil-overlap[a]	13.32
Critical concentration (g/dL)[a]	1.50

[a] Data taken from Lai and Chiang (2002).
[b] Data taken from Chen and Lai (2008).
[c] Data taken from Lin (2002).

2.2. Film preparation

Bilayer edible films were prepared by laminating films from two types of film-forming solutions according to the formulations shown in Table 2. Specifically, for the surfactant layer preparation, surfactant S-1170 was dissolved in a mixed solvents of degassed water and 95% alcohol ($v/v = 5/1$) at 80 °C to make a 2% surfactant solution (w/w). To enhance the surfactant layer lamination with the starch/dHG layer, various concentration of starch/dHG solutions (referred to SD) were added to the surfactant layer solutions, followed by homogenization at 4500 rpm for 2 min with a homogenizer (Polytron PT3000, Kinematica, Switzerland). 13–32.5 g of film-forming solutions for surfactant layer were cast onto a level circular Petri dish (135 mm, i.d.) and dried in a hood at 25 °C for 18 h. The film-forming solution of the second layer contained tapioca starch and dHG at a starch/dHG ratio of 1.7/0.3 to make a total solid content of 2% in deionized water, plus 15% glycerol based on the total solid. The film-forming solution was prepared by dissolving dHG in degassed deionized water with gentle heating (about 40 °C) and magnetic stirring, followed by the addition of glycerol and starch. The film-forming solution was then heated to 95 °C in a water bath, and maintained at 95 °C for 30 min with gentle magnetic stirring, followed by cooling at room temperature with gently magnetic stirring for 20 min to reduce air bubbles. Bilayer films were prepared by casting 40 g of starch/dHG solution onto the already prepared surfactant layer. Monolayer films with starch/dHG solution were also prepared by directly casting 40 or 58 g of starch/dHG solutions onto Petri dish for comparison purpose. After that, they were dried in a chamber of controlled temperature–humidity (GTH-072S, Giant Force Instrument Enterprise Co., Ltd, Taipei, Taiwan) at a relative humidity (RH) of 58% and 50 °C for 1 h, and sequentially at 25 °C for 72 h or until constant weight were obtained. Resulting films were then carefully peeled-off from the Petri dish and equilibrated at 25 °C, 57% RH for 72 h prior to further analysis.