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Structure and properties of moisture-resistant konjac glucomannan films coated with shellac/stearic acid coating

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ABSTRACT

A series of moisture-resistant konjac glucomannan films were prepared by coating shellac/stearic acid emulsion on deacetylated konjac glucomannan films (dKGM). The effect of stearic acid content on structure and properties of the coated films were investigated by field emission scanning electron microscopy (FE SEM), Fourier transform infrared spectroscopy (FT-IR), ultraviolet spectroscopy (UV), water vapor permeability (WVP), water uptake, water contact angle, and tensile testing. The results revealed that shellac in the coating adhered intimately to the surface of dKGM film, and provided a substrate for the dispersion of stearic acid which played an important role in enhancement of the moisture barrier properties and mechanical properties of the coated films. The WVP of the coated films decreased from 2.63×10^{-11} to 0.37×10^{-11} g/(m s Pa) and the water contact angle increased from 68° to 101.2° when stearic acid content increased from 0 wt% to 40 wt%, showing the potential applications in food preservation.

1. Introduction

It is well known that the natural polymers are of high safety and environmentally friendly. KGM, a high-molecular weight heteropolysaccharide, is composed of β-(1→4) linked D-glucose and D-mannose in the molar ratio of 1:1.6 with a low degree of acetyl groups at the side chain C-6 position (Li, Ji, Xia, & Li, 2012; Maeda, Shimahara, & Sugiyama, 1980). With good film-forming properties and health-protective functions, KGM shows promise in packaging and coating of food (Jia, Fang, & Yao, 2009). However, the applications of KGM films are limited by its hydrophilic and sensitive to moisture, due to a lot of hydroxyl groups in the repeating units of KGM (Xu, Luo, Lin, Zhuo, & Liang, 2009). In our previous work, based on the study of KGM structure (Jian, Zeng, Xiong, & Pang, 2011; Jian, Wang, Yao, & Pang, 2010), the KGM/curdlan blend films, with the water vapor permeability (WVP) value of 19.53×10^{-11} g/(m s Pa), have been prepared (Wu et al., 2012), showing better moisture-resistant properties than pure curdlan [21.50×10^{-11} g/(m s Pa)] but far from LDPE [0.19×10^{-11} g/(m s Pa)] (Phan The, Debeaufort, Luu, & Voilley, 2008). These results motivate us to carry out further research about the moisture-resistant films based on KGM, using an alternative method.

One way to achieve a moisture-resistant film with barrier against WVP is to coat or add some extra hydrophobic components to the film substrate, and then produce the coated film (Cao, Deng, & Zhang, 2006; Lu & Zhang, 2002; Lu, Zhang, & Xiao, 2004) or bilayer film (Anker, Berntsen, Hermansson, & Stading, 2002; Debeaufort, Quezada-Gallo, Delporte, & Voilley, 2000). In term of the coated films, the regenerated cellulose films coated with interpenetrating polymer networks (IPN) coating exhibit good water resistivity, unfortunately, the natural polymers in IPN coating are less than 30 wt% (Cao et al., 2006), failing to thoroughly utilize renewable resource. In term of the bilayer films, casting lipid onto the protein or polysaccharide films (Anker et al., 2002), the greasy surface, waxy taste and potential rancidity problem of lipids curb their use in food applications (Phan The et al., 2008), despite their WVP have significantly decreased. Hence in this work, one of the major tasks is trying to select other natural hydrophobic polymers as coating materials and coat them on KGM film.

Shellac, obtained by refining the secreton of *Kerria lacca*, is one of the few natural polymer allowed for coating purposes in food, owing to excellent film-forming, high gloss, and poor permeability to gases, acid and water vapor (Byun, Ward, &

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Whiteside, 2012; Farag & Leopold, 2009; Soradech, Nunthanid, Limmatvapirat, & Luangtana-Anan, 2012). It has also been used for the moisture protection of drugs in the pharmaceutical industry and found to decrease the WVP of edible films (Limmatvapirat et al., 2004; Luangtana-Anan, Nunthanid, & Limmatvapirat, 2010; Soradech, Limatvapirat, & Luangtana-Anan, 2013; Wang, Chen, & He, 2008). Shellac is comprised of polyesters and an ester with polyhydroxypolybasic acids, and insoluble in water but soluble in alcohol and alkaline solution (Limmatvapirat, Limmatvapirat, Puttipipatkhachorn, Nuntanid, & Luangtana-Anan, 2007; Luangtana-Anan, Limmatvapirat, Nunthanid, Wanawongthai, Chalongsuk, & Puttipipatkhachorn, 2007). It is well known that stearic acid, as a component of wax used by nature to create superhydrophobic lotus leaves, has been used in the field of moisture barrier due to its low surface energy (Wu, Pan, & Li, 2010). Moreover, with low cost, low toxicity, and biocompatibility, stearic acid could embed into regenerated cellulose film to form a micro–nano binary structure, resulting in the improvements of hydrophobicity (He, Xu, & Zhang, 2013). However, shellac/stearic acid composite coating has seldom been reported (Phan The et al., 2008; Soradech et al., 2013; Wang et al., 2008).

In this paper, in view of seldom reports on the preparation of the coated films based on KGM, we attempt to prepare a series of moisture-resistant deacetylated konjac glucomannan films (dKGM) coated with shellac/stearic acid, in which stearic acid content ranges from 5 up to 60 wt%. The effect of stearic acid content in the coating layer on interfacial and surface structure, moisture barrier properties, and mechanical properties of the resulting coated films were investigated in detail.

2. Materials and methods

2.1. Materials

Purified konjac glucomannan ($M_w = 3.4 \times 10^5$ g/mol) was purchased from San Ai Konjac Food Co., Ltd. (Sichuan, China). Shellac (food grade) was provided by Kunming Xilaike Bio-technology Co., Ltd. (Kunming, China), which was used without further purification. The stearic acid, Na_2CO_3, NaBr and 98% ethanol purchased from Sinopharm Group Chemical Reagent Co., Ltd. (China) were of analytical grade. Polyethylene glycol 400 (PEG 400) was chemical pure with purity ≥99.7%. Polyethylene film (PE, Top Group Co., Ltd, China) and qualitative filter papers (Hangzhou Tezhongzhiye Co., Ltd, China) were bought and used directly.

2.2. Preparation of the coated films

Deacetylated konjac glucomannan films (dKGM) were obtained after solubilization of 1 g of KGM flour in 100 g of deionized water at room temperature for 2.5 h under a 300 rpm stirring. Subsequently, 0.3 g of Na_2CO_3 was added, keeping stirring for 15 min. The film-forming solution was kept for 30 min under the same conditions without stirring prior to be spread onto polystyrene Petri dishes (PS, 150 mm × 25 mm) to provide a sheet with the thickness of about 5 mm and evaporated in an oven at 55 °C for 5 h to obtain dry films with the thickness of about 30 μm. Then, the films were washed exhaustively with distilled water to remove the residual Na_2CO_3 and evaporated again in an oven at 45 °C for 2 h.

The shellac/stearic acid coating was prepared by dissolving 12 g of shellac particles together with desired content of stearic acid, such as 0 wt%, 5 wt%, 20 wt%, 40 wt% and 60 wt%, in 100 g ethanol under a 300 rpm stirring for 60 min at room temperature. Then, 1.2 g of PEG 400 were added it under a stirring speed at about 5000 rpm (PT 3100 D, KINEMATICA, Switzerland) for 15 min. The resulting mixture solution, namely coating, which prepared from different stearic acid content (0–60 wt%) were denoted SSA0, SSA5, SSA20, SSA40, and SSA60, respectively. The coating was then coated on the both sides of dKGM by brush, and cured at 75 °C for 15 min. The coated films were referred to as dKGM-SSA0, dKGM-SSA5, dKGMSSA20, dKGM-SSA40, dKGM-SSA60, respectively. Before various characterizations, the resulting films were kept in a conditioning desiccator over saturated NaBr solution which fixed 57% RH at room temperature for more than one week to ensure the equilibrium of the water in the films.

2.3. Scanning electron microscopy

Film samples were observed by field emission scanning electron microscopy (FE SEM, Nova NanoSEM230, FEI, America). The films were frozen in liquid nitrogen, immediately snapped, and then dried for the FE SEM observation. The surface of the films was sputtered with platinum for 2.5 min and then observed with 5 kV accelerating voltage.

2.4. Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FT-IR) was carried out with a FT-IR spectrometer (VERTEX 70, Bruker, Germany) in the wavelength range from 4000 to 400 cm^{-1}. The powdered and dried samples were obtained, and the test specimens were prepared by the KBr disk method.

2.5. Ultraviolet spectroscopy

Ultraviolet spectroscopy of films, with thickness of about 38 μm, were carried out with a ultraviolet–visible spectrophotometer (Lambda 800 UV/VIS, Perkin Elmer, America) in the wavelength range from 200 to 800 nm.

2.6. Water vapor permeability determination

Water vapor permeability (WVP) at a relative humidity differential was measured using China National Standard GB 1037-88 (1989) modified by inversing its RH differential, homologous to the ASTM E96-80 (1980). All films used were fixed between two Teflon rings on the top of the glass cell containing distilled water of which the relative humidity is 99% at 25 °C. Test cell was introduced into a climate-controlled chamber (GSP-9160MBE, Shanghai Boxunshiye Co., Ltd., China) regulated at 57% RH and 23 °C; 11% RH and 23 °C or 57% RH and 38 °C. Thus, three relative humidity and temperature differentials (gradients) were used: 57–99% and 23 °C; 11–99% and 23 °C; 57–99% and 38 °C, which mimic a product exposed to different ambient.

Test cell was periodically weighted up to a constant weight variation rate. WVP [g/(m s Pa)] was calculated according to the following equation:

$$\mathrm{WVP} = \frac{\Delta m \times d}{A \times t \times \Delta p}$$

where Δm (g) is the amount of water vapor movement across the film (weight loss); d (mm) is the film thickness; A (mm^2) is the area of the exposed film; Δp (Pa) is the actual difference in partial water vapor pressure between the two sides of the film specimen; t (s) is the time during which a stable weight gain occurred. At least three replicates of each film type were tested for WVP.

2.7. Water uptake measurement

The water uptake of the films was measured according to the procedure described by He, Xu, and Zhang (2013). The films used