International Journal of Biological Macromolecules xxx (2018) xxx–xxx

Contents lists available at ScienceDirect

International Journal of Biological Macromolecules

journal homepage: http://www.elsevier.com/locate/ijbiomac

# Mechanical and barrier properties of corn distarch phosphate-zein bilayer films by thermocompression

Haitao Sun [a,b,*], Xinru Shao [a,b], Ruiping Jiang [a,b], Zhimin Shen [a], Zhongsu Ma [c]

[a] College of Food Science and Engineering, Tonghua Normal University, No. 950 Yucai Road, Tonghua 134000, Jilin, PR China
[b] Changbai Mountain Edible Plant Resources Development Engineering Center, Tonghua Normal University, No. 950 Yucai Road, Tonghua 134000, Jilin, PR China
[c] College of Food Science and Engineering, Jilin University, No. 5333 Xi'an Road, Changchun 130062, Jilin, PR China

ARTICLE INFO

*Article history:*
Received 18 February 2018
Received in revised form 28 June 2018
Accepted 12 July 2018
Available online xxxx

*Keywords:*
Bilayer films
Corn distarch phosphate-zein
Thermocompression

ABSTRACT

Corn distarch phosphate-zein bilayer films (C-Z) fabricated from corn distarch phosphate-based films (C) laminated on zein-based films (Z) by thermocompression. The strong interaction between starch and zein molecules was formed by hydrogen bonding, which resulted in good thermal stability of bilayer films. Moreover, bilayer films exhibited better mechanical properties and ductility than monolayer Z films, and concomitantly enhanced the moisture barrier and oxygen barrier for monolayer C films. The tensile strength (TS) and elongation at break (EAB) of the C-Z bilayer films (the ratio C:Z was 6:4) increased by 74.04% and 348.13% over the Z films, respectively. Compared with C films, the water vapor permeability (WVP) and oxygen permeability (OP) of the C-Z bilayer films (the ratio C:Z was 6: 4) decreased by 31.53 and 24.26%, respectively.



## 1. Introduction

In recent years, the interest in the application of biodegradable food packaging materials has grown due to concern over traditional petroleum based plastic materials full degradation requires a long period of time [1]. In order to lessen environmental pollution, biodegradable, renewable, environmental-friendly and edible biopolymers should be considered in the development of new packaging materials [2]. These biopolymers are obtained from different agro industrial waste and byproducts (polysaccharides, proteins and lipids), and considered as ideal alternatives for non-biodegradable traditional petroleum based plastic [3].

In many choices, starch has been considered as a cheap and promising substitute for packaging applications. Starch derived from different common source, such as corn, wheat, potatoes, pea, and cassava, it is abundant and safe as packaging materials in food and pharmaceutical industry [4]. Over the past decade, starch-base film is being extensively studied due to its good ability for film forming (good flexibility, good light transmittance, and easy to be peeled from the film applicator). Unfortunately, starch-base film is sensitive to environmental dryness and humidity, the shape and properties will be changed greatly at different temperatures and humidity in packaging and storage [5]. Therefore, in order to be suitable for packaging, transport and storage, the poor barrier properties of starch-base film are required to be improved [6]. To overcome this limitation, the starch-base film was strengthened with other polymers.

Zein, a by-product obtained from corn starch processing, is prepared from corn protein flour. Zein is particularly rich in hydrophobic and neutral amino acids as well as some sulfur-containing amino acids, but lack of polar amino acids or ionizable amino acids. Due to its large number of hydrophobic groups, zein is soluble in 60%–95% aqueous ethanol, yet is insoluble in pure water [7]. Zein is well-known for its film forming properties because of its unique amino acid composition, and has been widely used in food packaging materials [8–11]. Pure zein films have good water barrier properties, but their mechanical properties are relatively poor. In order to overcome these deficiencies, blend zein films with other biodegradable biopolymers has been widely studied, and the zein provided good potential for the production of blend films [12–14]. For example, several studies have been evaluated composite zein-chitosan edible films, better barrier and mechanical properties were obtained using zein [15]. And the water vapor barrier and mechanical properties of the whey protein isolate films were significantly improved by addition of zein nanoparticles [16]. Wang et al. prepared konjac glucomannan/zein blend films, the hydrophobicity of blend films were significantly increased compare with pure konjac glucomannan film, and other properties such as mechanical properties, thermal stability, water vapor permeability and oxygen permeability were also found to be improved [17].

Lots of attempts have been made to improve the mechanical properties and barrier properties of the biopolymer films, such as chemical cross-linking, enzymatic, physical modification and lamination

* Corresponding author at: College of Food Science and Engineering, Tonghua Normal University, No. 950 Yucai Road, Tonghua 134000, Jilin, PR China.
*E-mail address:* sunhaitaoth@126.com (H. Sun).

https://doi.org/10.1016/j.ijbiomac.2018.07.069
0141-8130/

methods [18]. The preparation of bilayer films is a promising option to improve the properties of the films. Both corn distarch phosphate and zein are biodegradable polymers, and bilayer combination can complement their film forming properties. Solvent casting has been the most widely used method of biopolymers films preparation, which involves the disadvantages of deform, delaminate and crack over time. In this context, the thermocompression method is a viable alternative for producing thermoplastic bilayer films, which is less reported. During the thermocompression of films, the combination of heat and pressure allows for producing integrally compact and uniform bilayer films without polymer solubilization [6,19]. In this sense, the combination of corn distarch phosphate-based films (C films) and zein-based films (Z films) as corn distarch phosphate-zein bilayer films (C-Z films), can be a feasible and interesting approach to develop new economical and ecological materials.

The aim of this work was the development of C-Z films fabricated from C films laminated on Z films by thermocompression. The characterize was conducted using scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), thermal gravity analysis (TGA). Further, mechanical properties and barrier properties of films were researched.

## 2. Materials and methods

### 2.1. Film-forming materials

Corn distarch phosphate was obtained from Dahua Starch Co., Ltd. (Changchun, China). Zein powder was supplied by Sigma-Aldrich (St. Louis, MO, USA). Nanocrystalline corn straw cellulose (NCSC) was made in the laboratory according to the method described in literature [20]. Polyethylene glycol (PEG-400), ethanol and glycerol (Gly, $CH_8O_3$ ≥ 99%) and other chemicals used were of analytical grades.

### 2.2. Film preparation

C films were prepared by solvent casting technique as previously described by Sun et al. [20]. Z films were obtained by melt blending and casting. Specifically, zein (10.0% w/w) was dispersed in an aqueous solution of ethanol (80.0% v/v) under magnetic stirring at room temperature for 10 min. The film-forming solutions (FFSs) were prepared by adding Gly at 0.6% (w/w) and PEG at 0.3% (w/w). FFSs were homogenized with a stirrer at 70 °C for 20 min and the air bubbles were removed by vacuum degassing. Subsequently, FFSs were cast in the plexiglass film applicator (20 cm × 20 cm), which were placed in a dryer (GZX-9140, Shanghai Boxun Instruments Co., Ltd., Shanghai, China) at 50 °C for 1.5 h to allow for solvent evaporation and film formation.

Fig. 1 shows the preparation process of C-Z bilayer films. C-Z bilayer films fabricated from C films laminated on Z films by thermocompression (the ratio C:Z was 7:3, 6:4, 5:5, 4:6 and 3:7), at 120 °C for 20 s. The films were placed in a constant temperature and humidity equipment (SPX-250, Changzhou Noki Instruments Co., Ltd., Changzhou, China) at 25 °C and 60% RH for 24 h prior to performing the analysis of thermal, and mechanical and barrier properties were measured.

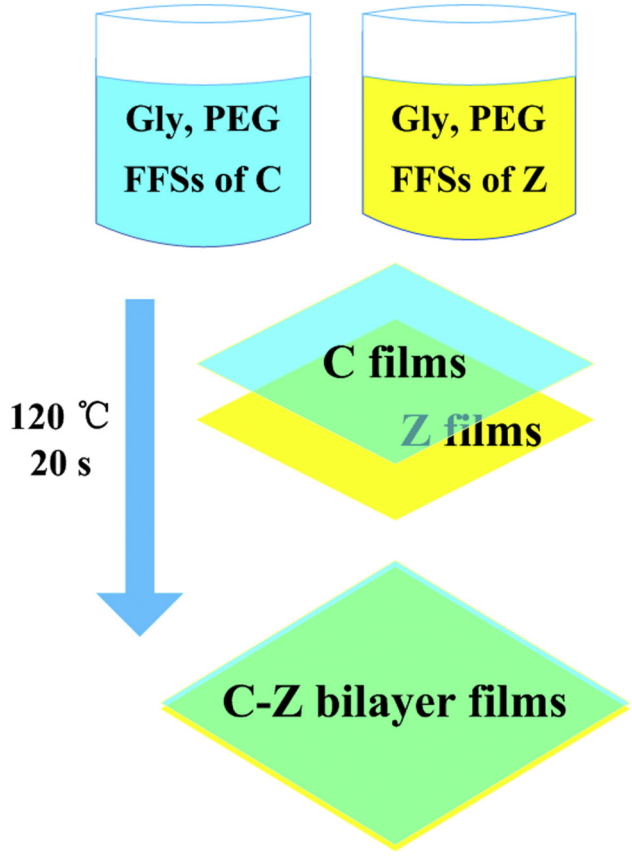


**Fig. 1.** Fabricated process for bilayer C-Z films.

### 2.3. Film characterization

#### 2.3.1. The appearances and scanning electron microscopy (SEM)

The surface color of the films was measured using a colorimeter (Lovibond RT-300, Reflactance Tintometer, United Kingdom) with 8 mm diameter. The color was expressed as $L$ (lightness), $a$ (redness/greenness) (±) and $b$ (yellowness/blueness) (±) value [21]. The machine was calibrated using a white standard plate ($L^* = 94.1 \pm 0.08$, $a^* = -1.39 \pm 0.01$, and $b^* = -0.97 \pm 0.02$). The total color difference ($\Delta E$) was calculated as follows:

$$\Delta E = \sqrt{(L - L*)^2 + (a - a*)^2 + (b - b*)^2}$$

The microstructural analysis of surface and cross-section of films was carried out by cold field emission scanning electron microscope (S-3000N, Japan Electronics Co., Ltd., Japan). The films were fixed on copper stubs using double-sided tape, sputtered with a thin layer of gold, and examined using an accelerating voltage of 20 kV. The magnifications of surface and cross-section were 5000× and 500×, respectively.

#### 2.3.2. X-ray diffraction (XRD)

The crystalline structures of films were identified by XRD (DX-2700 X-ray diffraction, Haoyuan Instrument Co., Ltd., China) with a Cu radiation. Operation was carried out at 40 kV and 40 mA, scanning range from 5 to 50°. The degree of crystallinity ($C_D$) was calculated as follows:

$$C_D\% = \frac{A_c}{A_c + A_a} \times 100$$

where $A_c$ is the area of crystalline phase and $A_a$ is the area of amorphous phase.

#### 2.3.3. Fourier transform infrared spectroscopy (FTIR)

Attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectroscopy measurements were performed by a spectrometer (IS50, Thermo Nicolet Corporation, American) in the range of 4000 $cm^{-1}$ to 550 $cm^{-1}$ with a resolution of 4 $cm^{-1}$ and 16 scans.

Please cite this article as: H. Sun, et al., Mechanical and barrier properties of corn distarch phosphate-zein bilayer films by thermocompression, (2018), https://doi.org/10.1016/j.ijbiomac.2018.07.069