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Enhanced water resistance properties of bacterial cellulose multilayer films by incorporating interlayers of electrospun zein fibers

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ABSTRACT

In this work, we developed multilayer bacterial cellulose (BC)-zein films based on the strong BC film as the outer layers and the electrospun zein fibers as the inner layer, to improve the water resistance properties of hydrophilic BC films. The water resistance properties were evaluated by dynamic water absorption measurement and mung beans storage test. The obtained results showed that the incorporation of electrospun zein fibers made the relatively thin and flexible multilayer films become stiffer, while the zein interlayer did not markedly affect the thermal stability and surface properties of films. Compared to pure BC films, the BC-zein films exhibited significantly better water resistance properties, especially under longer zein deposition time (90 and 120 min). This improvement could be mainly due to the inherent hydrophobicity of zein protein. These findings provide the possibility of adopting a multilayer film strategy for the development of BC packaging films with enhanced water resistance properties by incorporating a high barrier interlayer of electrospun zein fibers.

1. Introduction

Bacterial cellulose (BC), synthesized by *Acetobacter xylinum* species, is a natural, renewable, and biodegradable material, which consists of random assembled nanofibrils less than 100 nm wide (Hestrin & Schramm, 1954; Okiyama, Motoki, & Yamanaka, 1993; Okiyama, Shirae, Kano, & Yamanaka, 1992). In comparison with plant derived cellulose, BC has distinctive advantages, although both of them have the same chemical structure. For instance, BC has a higher crystallinity, polymerization degree and water holding capacity, since it can be obtained in a pure form, containing no lignin, pectin, or hemicelluloses (Iguchi, Yamanaka, & Budhiono, 2000; Klemm, Schumann, Udhardt, & Marsch, 2001). In addition, BC shows a higher and more stable mechanical strength due to its ultrafine network structure. Owing to its unique properties, BC has attracted increasing interest for various applications in paper-making (Basta & El-Saied, 2009; Iguchi et al., 2000), food (Shi, Zhang, Phillips, & Yang, 2014), electronics (Nogi & Yano, 2008; Shah & Brown, 2005), biomedicine (Fu, Zhang, & Yang, 2013; Klemm et al., 2001; Svensson et al., 2005; Zaborowska et al., 2010) and many others. Among these, the literature about the application of BC in the food industry are relatively limited (Okiyama, Motoki, & Yamanaka, 1993, 1992; Iguchi et al., 2000; Shi et al., 2014). It is well known that the first use of BC in the food industry was in the manufacture of Nata, a traditional dessert in Southeast Asia (Iguchi et al., 2000). Moreover, as a type of dietary fiber, BC has been classified as "generally recognized as safe" (GRAS), and was approved for marketing by the US Food and Drug Administration (FDA) in 1992 (Shi et al., 2014). Recently, a review from Shi et al. reported the potential applications for BC in foods (Shi et al., 2014). For example, BC could be used to improve the rheology of food as a thickening, stabilizing, gelling or suspending agent, and BC also could produce low-calorie and low-cholesterol food products (Okiyama, Motoki, et al., 1992; Okiyama et al., 1993; Paximada, Koutinas, Scholten, & Mandala, 2016; Shi et al., 2014).

Another promising field of application for BC in the food industry is the utilization of BC film as edible packaging materials to improve the quality and safety of food products (Falguera, Quintero, Jiménez, Muñoz, & Ibarz, 2011; Shi et al., 2014) since the BC films exhibit sufficient mechanical properties, edibility, and

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biodegradability. However, the BC films show poor water resistance properties due to the hydrophilic nature of cellulose, which is the main drawback in many packaging applications, especially in the food sector. In order to overcome this issue, several strategies, such as the hydrophobic modification of BC surface and the combination with other barrier polymers to produce composite films, have been explored (Ifuku et al., 2007; Lee, Blaker, & Bismarck, 2009; Lee et al., 2011; Stoica-Guzun et al., 2011; Tomé et al., 2010, 2011). Indeed, the regenerated BC films exhibit significantly improved water resistivity by using these strategies; however, the safety concerns have to be raised when using these modified BC films as edible films in food packaging. For example, it is known that surface hydrophobization of BC often involves the use of organic chemicals, which are not environmentally friendly and can be toxic, such as various organic acids, anhydrides, and hexanoyl chloride (Ifuku et al., 2007; Lee et al., 2011; Tomé et al., 2010, 2011). In addition, the synthetic or semi-synthetic polymers such as ethylene vinyl alcohol, polyvinyl alcohol and polyamides are commonly used in the fabrication of composite BC films (Lee et al., 2009; Li, Mascheroni, & Piergiovanni, 2015; Stoica-Guzun et al., 2011). Therefore, more safe and food-grade strategies, which do not involve any toxic chemicals or just fabricate composite materials with barrier biopolymers, are required to improve the water resistant properties of BC films, to extend their application as edible films in food packaging.

In recent years, the strategy that make use of multilayer film systems has attracted increasing interest for food packaging applications due to its efficiency in enhancing the barrier properties of materials (Fabra, Busolo, López-Rubio, & Lagaron, 2013). By using this technology, it is feasible to obtain maximum barrier performance by making the materials in the outer layers and the inner layer with different barrier properties assemble into the most efficient form (Fabra, Busolo, et al., 2013; Lagaron, 2011). Hence, based on this strategy, we attempt to fabricate multilayer BC films to enhance their water resistant properties. Among commonly used biopolymers in food industry, we select zein, a major protein of corn, as the materials to form the inner layer of multilayer films. It is known that zein is an edible, abundant, inexpensive, and renewable biopolymer (Shukla & Cheryan, 2001). Different from most of the natural biopolymers like whey proteins, soy proteins, and most polysaccharides, zein is insoluble in water because it contains over 50% hydrophobic amino acids (Shukla & Cheryan, 2001). The inherent hydrophobicity of zein endows it with certain specific interesting properties in terms of water resistance, thermal resistance or viscosity. The zein-based films also show lower water vapor permeability with good mechanical properties, as compared to films produced by other proteins and polysaccharides (Beck, Tomka, & Waysek, 1996; Shukla & Cheryan, 2001; Zhang et al., 2015). Therefore, zein interlayers sandwiched between BC films are expected to provide the final multilayer films with overall improved water resistant properties. However, highly hydrophilic BC and hydrophobic zein protein are thermodynamically immiscible, which would result in the poor adhesion between the two materials, thus weakening the properties of final films. Recently, Lagaron and coworkers reported that, through the use of electrospinning technique, multilayer biopolyester films containing an electrospun zein fiber interlayer showed good adhesion between the layers, and the obtained multilayer films had significantly improved water and oxygen barrier properties (Busolo, Torres-Giner, & Lagaron, 2009; Fabra, López-Rubio, & Lagaron, 2013). They attributed this improvement to the lower permeabilities of water vapor and oxygen of zein protein, as well as to the dense structure of multilayer films. The production of zein nanofibers through electrospinning has been extensively reported recently, and the electrospun zein nanofibers with diameters ranging from less than 100 nm to above 1 μm can be obtained by modifying the process parameters of electrospinning (Torres-Giner, Gimenez, & Lagaron, 2008). Based on these previous findings, we thus attempt to increase the adhesion between BC and zein layers by using the interlayer of electrospun zein fibers and thus enhance the efficiency of the final multilayer films.

Therefore, in this work, we aim to improve the water resistance properties of hydrophilic BC films by adopting a multilayer film strategy, and electrospun zein fibers were selected as the interlayer for the multilayer films due to good adhesion and inherent hydrophobicity of zein protein. The influence of incorporating electrospun zein interlayers on the mechanical and thermal properties of films was investigated. The water resistance properties of BC-zein multilayer films were evaluated by dynamic water absorption measurement and mung beans storage test.

2. Materials and methods

2.1. Materials

Purified bacterial cellulose (BC) pellicles with a thickness of around 5.0 mm were kindly provided by Hainan Guangyu Biotechnology Co., Ltd., China. These pellicles were further treated with 0.2 M NaOH at 80 °C for 30 min, and then were thoroughly washed with running distilled water until the pH was reduced to 7.0. Zein was purchased from Sigma Chemical Co. (St. Louis, MO, USA). Mung beans were purchased from a local market (Guangzhou, China). All other chemicals used were of analytical grade.

2.2. Preparation of multilayer BC-zein films

2.2.1. Preparation of BC films

The preparation of multilayer BC-zein films was divided into three steps, as shown in Fig. 1. First, to obtain BC films, the wet BC pellicles were cut into pieces of 10 cm by 10 cm, and then pressed for 5 min at room temperature (25 °C) and 0.4 MPa of pressure to squeeze out most remaining water. The resulting gel-like films were placed in a semi-automatic sheet former (Rapid-Köthen, Austria) at 90 °C and 0.1 MPa for 10 min. After that, the dry BC films were obtained.

2.2.2. Preparation of electrospun zein interlayers through electrospinning

Zein ultrathin fibers were obtained through the electrospinning of 30 wt% of zein in an 80% v/v ethanol solution (SS-2535DC; Ucalery, Beijing, China), as described previously (Torres-Giner et al., 2008). The zein solutions were prepared under magnetic stirring for 1 h at room temperature (25 °C) and then placed in a 5 mL plastic syringe. The syringe was connected through PTFE tubes to a stainless steel needle (0.9-mm outer diameter, 0.8-mm inner diameter). The electrospinning was carried out at an applied voltage of 12–14 kV with a flow rate of 0.06 mL/min. The distance between the tip of syringe needle and the aluminum foil wrapped on the winding drum was kept at 10 cm. The collecting drum was rotated at 1200 rpm. The electrospun zein fibers were directly collected onto dry BC films, which were attached onto the surface of aluminum foil. The movement of spinneret was controlled to make all the fibers deposited inside the BC films. Three different deposition times (60, 90, and 120 min) were evaluated to investigate the influence of different amounts of zein fibers on the tensile and water resistant properties of BC films. The electrospinning process was performed at room temperature (25 °C) and 60% relative humidity (RH) by having the equipment enclosed in a specific chamber with temperature and humidity control.